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DEVELOPMENT DOCUMENT FOR EFFLUENT LIMITATIONS GUIDELINES AND NEW SOURCE PERFORMANCE STANDARDS FOR THE PHOSPHORUS DERIVED CHEMICALS SEGMENT OF THE PHOSPHATE MANUFACTURING POINT SOURCE CATEGORY

ENVIRONMENTAL PROTECTION AGENCY

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Effluent limitations guidelines were developed as a result of this study, defining the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the best available technology economically achievable which must be achieved by existing point sources by July 1, 1977, and July 1, 1983, respectively. The standards of performance for new sources were also defined.

The best practicable control technology currently available allows a discharge after suitable treatment for the manufacture of phosphorus (and ferrophosphorus), phosphorus trichloride, phosphorus oxychloride and food grade calcium phosphate. The 1977 limitations prohibit discharge of process waste water pollutants for the manufacture of the remaining chemicals.

Application of the best available technology economically achievable and best demonstrated technology would enable all the manufacturing operations for the three subcategories to achieve no discharge of waste water pollutants.

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SECTION I

CONCLUSIONS

For the purpose of establishing effluent limitations guidelines and standards of performance, the phosphate manufacturing point source category was divided into the phosphorus production, the phosphorus consuming, and the phosphate subcategories.

Phosphorus and phosphoric acid (furnace acid) production were included in this study because they are necessary prerequisites to phosphate synthesis. It is also appropriate from a technical standpoint to include these chemicals in this study rather than in the inorganic chemical point source category. Other phosphorus consuming chemicals such as PCl_3 and P_2O_5 were included for the same reasons. Processes that manufacture phosphates as fertilizers are regulated by the fertilizer manufacturing regulations.

The phosphorus-production subcategory of the industry is characterized by large quantities of raw process wastes, including highly deleterious phossy water and highly-acidic scrubber and quenching waste waters, both containing large quantities of fluorides, other dissolved solids, and suspended solids. Through a combination of in-process controls and end-of-process treatment, several plants within this segment have achieved zero discharge of phossy water, two have achieved zero discharge of other process waste waters, and one has achieved zero discharge of any waste water during normal periods of rainfall. Plants now demonstrate abatement practices resulting in 97 percent or greater reduction in the raw waste load before discharge, and the total recycle of process water without any discharge has been demonstrated using the best practicable control technology.

The phosphorus-consuming subcategory of the industry is characterized by the absence of direct process waste water; the chemicals produced are readily hydrolyzed so that the processes are essentially dry. However, just because the products are readily hydrolyzed, water is universally used for air pollution abatement scrubbing of tail gases, for periodic cleaning of reaction vessels, and for the general washing of shipped containers, all resulting in acidic waste waters. In addition, water is used in protecting and transferring the raw material, elemental phosphorus, and phossy water is therefore a raw waste from this segment. Except for the manufacture of dry-process phosphoric acid (where in-process control has been demonstrated to achieve zero discharge of aqueous wastes), this segment has not yet achieved sufficient reduction of effluents. The application, however, of currently available technology is shown by this study to permit total recycle of waste waters (and so zero discharge) for the manufacture of P_2O_5 and P_2S_5, and to achieve the neutralization and removal of most suspended solids before discharge for the manufacture of PCl_3 and $POCl_3$. The latter two processes are more expensive but still economically achievable technologies and are available for treating the chlorides so as to achieve zero discharge.

The phosphate segment of the industry, i.e., the group of chemicals manufactured from phosphoric acid, is characterized by acids and by finely-divided solids in the raw aqueous wastes. Several plants have already achieved zero discharge by in-process controls and by end-of-process treatment; and this study shows how this segment may achieve zero discharge by applying currently available practicable technology. Outside contamination of the process waste water resulting from the manufacture of food grade calcium phosphate may prevent its reuse at existing plants, and a discharge after suitable treatment has been allowed.

The general conclusion reached is that the industry has already solved its most serious raw waste problem; that is, the abatement of water pollution from phosphorus-producing facilities. The remainder of the industry, made up of much smaller-volume plants, has lagged behind in effluent reduction, but technology is available to make the entire industry notable.

SECTION II

RECOMMENDATIONS

The recommended effluent limitations guidelines based on best practicable control technology currently available are no discharge of process waste water pollutants to navigable waters for the manufacture of the following chemicals:

- Phosphorus Consuming Subcategory
    - Phosphoric Acid (Dry Process)
    - Phosphorus Pentoxide
    - Phosphorus Pentasulfide
- Phosphate Production Subcategory
    - Sodium Tripolyphosphate
    - Calcium Phosphates (Animal Feed Grade)

The recommended effluent limitations for this technology for phosphorus (and ferrophosphorus), phosphorous trichloride, phosphorous oxychloride and food grade calcium phosphate are given in Table 1.

The above guidelines apply to the maximum average of daily values for any period of 30 consecutive days. The maximum for any one day is twice the consecutive 30 day average value. The pH limitation must be met at all times. It is recommended that noncontact cooling water be allowed to be discharged. Effluent limitations for this waste stream are expected to be covered in future studies. For the purposes of this report, process water is defined as any water that comes into direct contact with any raw material, intermediate product, by-product, or gas or liquid that has accumulated such constituents.

The recommended effluent limitations guidelines based on best available technology economically achievable is no discharge of process waste water pollutants for the manufacture of the following chemicals:

- Phosphorus Consuming Subcategory
    - Phosphorus (and Ferrophosphorus)
- Phosphorus Consuming Subcategory
    - Phosphoric Acid (Dry Process)
    - Phosphorus Pentoxide
    - Phosphorus Pentasulfide
    - Phosphorus Trichloride
    - Phosphorus Oxychloride
- Phosphate Subcategory
    - Sodium Tripolyphosphate
    - Calcium Phosphates (Food Grade)
    - Calcium Phosphates (Animal Feed Grade)

The recommended new source performance standards are the same as the above recommended best available technology economically achievable.

TABLE 1.

Recommended Best Practicable Control Technology Currently Available for the Manufacture of Phosphorus (and Ferrophoshorus), Phosphorus Trichloride, Phosphorus Oxychloride and Food Grade Calcium Phosphate. (Process Water)

The recommended effluent limitations guidelines based on best practicable control technology currently available for process water for the manufacture of PCl_3 and $POCl_3$ are:

Average of daily values for thirty consecutive days shall not exceed

	Phosphorus and Ferrophosphorus	Phosphorus Trichloride	Phosphorus Oxychloride	Food Grade Calcium Phosphate
Total Suspended Nonfilterable Solids kg/kkg	0.5	0.7	0.15	0.06
Total Phosphorus kg/kkg	0.15	0.8	0.17	0.03
Fluoride kg/kkg	0.05			
Arsenic kg/kkg		0.00005		
pH	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0

SECTION III

INTRODUCTION

PURPOSE AND AUTHORITY

Section 301(b) of the Act requires the achievement by not later than July 1, 1977, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best practicable control technology currently available as defined by the Administrator pursuant to Section 304(b) of the Act. Section 301(b) also requires the achievement by not later than July 1, 1983, of effluent limitations for point sources, other than publicly owned treatment works, which are based on the application of the best available technology economically achievable which will result in reasonable further progress toward the national goal of eliminating the discharge of all pollutants, as determined in accordance with regulations issued by the Administrator pursuant to Section 304(b) of the Act. Section 306 of the Act requires the achievement by new sources of a standard of performance providing for the control of the discharge of pollutants which reflects the greatest degree of effluent reduction which the Administrator determines to be achievable through the application of the best available demonstrated control technology, processes, operating methods, or other alternatives, including, where practicable, a standard permitting no discharge of pollutants.

Section 304(b) of the Act requires the Administrator to publish within one year of enactment of the Act, regulations providing guidelines for effluent limitations setting forth the degree of effluent reduction attainable through the application of the best control measures and practices achievable including treatment techniques, process and procedure innovations, operation methods and other alternatives. The regulations proposed herein set forth effluent limitations guidelines pursuant to Section 304(b) of the Act for the phosphate manufacturing point source category.

Section 306 of the Act requires the Administrator, within one year after a category of sources is included in a list published pursuant to Section 306(b)(1)(A) of the Act, to propose regulations establishing Federal standards of performances for new sources within such categories. The Administrator published in the Federal Register of January 16, 1973 (38 F.R. 1624), a list of 27 source categories. Publication of the list constituted announcement of the Administrator's intention to establish, under Section 306, standards of performance applicable to new sources within the phosphate manufacturing source category.

SUMMARY OF DEVELOPMENT METHODS

The Environmental Protection Agency has determined that a rigorous approach including plant surveying and verification testing is necessary for the promulgation of effluent standards from industrial sources. A systematic approach to the achievement of the required guidelines and standards includes the following:
(a) Categorization of the industry and determination of those industrial categories for which separate effluent limitations and standards need to be set;
(b) Characterization of the waste loads resulting from discharge within industrial categories and subcategories;
(c) Identification of the range of control and treatment technology within each industrial category and subcategory;
(d) Identification of those plants having the best practical technology currently available (notable plants); and
(e) Generation of supporting verification data for the best practical technology including actual sampling of plant effluents by field teams.

The culmination of these activities is the development of the guidelines and standards based on the best practicable current technology.
This report describes the results obtained from application of the above approach to the phosphate manufacturing industry, defined for the purpose of this study as the following list of products:

Elemental Phosphorus and Ferrophosphorus
Dry-Process Phosphoric Acid
Phosphorus Pentoxide
Phosphorus Pentasulfide
Phosphorus Trichloride
Phosphorus Oxychloride
Sodium Tripolyphosphate
Calcium Phosphates (Non-Fertilizer)

The effluent limitations guidelines and standards of performance proposed herein were developed in the following manner. The point source category was first subcategorized for the purpose of determining whether separate limitations and standards are appropriate for different segments within a point source category. Such subcategorization was based on raw material used, product produced, manufacturing process employed, and other factors. The raw waste characteristics for each subcategory were then identified. This included an analysis of (1) the source and volume of water used in the process employed and the sources of waste and waste waters in the plant, and (2) the constituents (including thermal) of all waste waters including toxic constituents which result in taste, odor, and color in water or aquatic organisms. The constituents of waste waters which should be subject to effluent limitations guidelines and standards of performance were identified.

The full range of control and treatment technologies existing within each subcategory was identified. This included an identification of each distinct control and treatment technology, including both in-plant and end-of-process technologies which are existent or capable of being designed for each subcategory. It also included an identification in terms of the number of constituents (including thermal). The chemical, physical, and biological characteristics of pollutants of the effluent level resulting from the application of each of the treatment and control technologies and the required implementation time were also identified. In addition, the non-water quality environmental impact, such as the effects of the application of such technologies on other pollution problems, including air, solid waste, noise and radiation, were also identified. The energy requirement of each of the control and treatment technologies was identified as well as the cost of the application of those technologies.

The information as outlined above was then evaluated to determine what levels of technology constituted the best practicable control technology currently available, the "best available technology economically achievable" and the "best available demonstrated control technology, processes, operating methods, or other alternatives." In identifying the technologies, various factors were considered. These included the total cost of application of technology in relation to the effluent reduction benefits to be achieved from the application, the age of equipment and facilities involved, the process employed, the engineering aspects, process changes, non-water quality environmental impact (including energy requirements), and other factors.

The data for identification and analysis were derived from a number of sources. These sources included EPA research information, published literature, previous EPA technical guidance for inorganic chemicals, alkali and chlorine industries, qualified technical consultation, and on-site visits and interviews at notable manufacturing plants throughout the United States. All references used in developing the guidelines for effluent limitations and standards of performance for new sources reported herein are included in Section XIII of this document. Five companies in the phosphate manufacturing industry were contacted. A breakdown of the data base is listed below:

Chemical	Number of Plants in Data Base			
	Literature	Inspected	Sampled	Permit Application
P_4	1	3	2*	2
H_3PO_4		2	1*	2
P_2O_5		1	1	1
P_2S_5		2	2	2
PCl_3		2	2	2
$POCl_3$		2	2	2
$Na_5P_3O_{10}$		2	1*	1
Calcium Phosphates				
(Food Grade)		1	1	1
(Feed Grade)		1	1	1

*Includes verification of plants with no discharge.

In addition much information was obtained from plant personnel at the time of plant inspections, plant sampling, and company discussions.

GENERAL DESCRIPTION OF THE INDUSTRY

The industry covered by this document is the phosphate manufacturing point source category. It is more descriptively termed the nonfertilizer phosphorus industry. The following chemicals covered by SIC 2819 were studied:

- phosphorus
- ferrophosphorus
- phosphoric acid (dry process)
- phosphorus pentoxide
- phosphorus pentasulfide
- phoshporus trichloride
- phosphorus oxychloride
- sodium tripolyphosphate
- calcium phosphates (food grade)
- calcium phosphates (animal feed grade)

Other phosphorus and phosphate chemicals are expected to be covered at a later time.

The flow of materials in the phosphate manufacturing industry is depicted in Figure 1. This industry is almost entirely based on the production of elemental phosphorus from mined phosphate rock. The economics have dictated that the phosphorus production facilities be located at the sources of the raw material, which are in three areas in the United States: Tennessee, the Idaho-Montana area, and Florida. The key in-plant siting decision is the relative weights of phosphate rock, elemental phosphorus and phosphoric acid (about 10:1:4). Hence, the rock is processed close to the mine and the acid is produced close to its consumption point; the relatively low-weight elemental phosphorus is almost universally the form shipped from place to place.

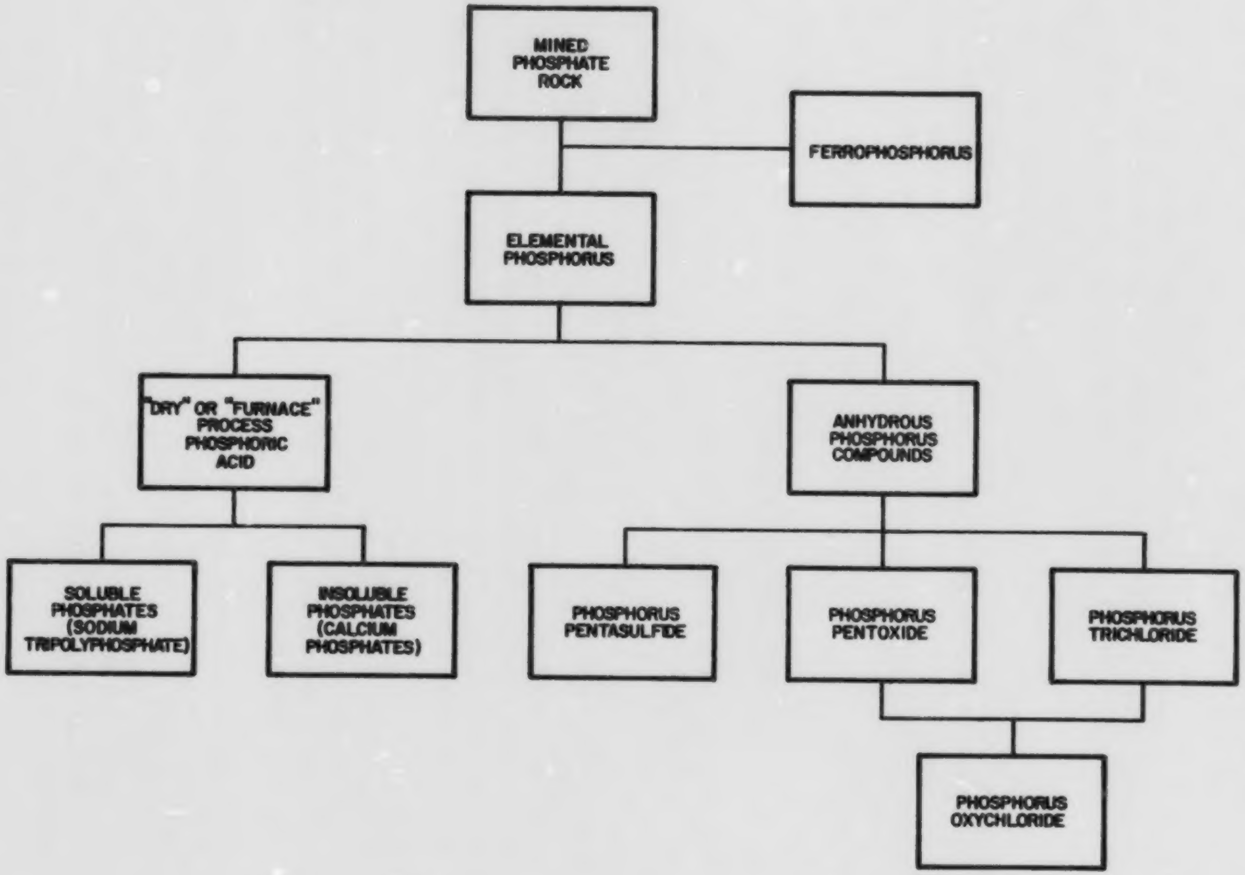
MINED PHOSPHATE ROCK
FERROPHOSPHORUS
ELEMENTAL PHOSPHORUS
"DRY" OR "FURNACE" PROCESS PHOSPHORIC ACID
ANHYDROUS PHOSPHORUS COMPOUNDS
SOLUBLE PHOSPHATES (SODIUM TRIPOLYPHOSPHATE)
INSOLUBLE PHOSPHATES (CALCIUM PHOSPHATES)
PHOSPHORUS PENTASULFIDE
PHOSPHORUS PENTOXIDE
PHOSPHORUS TRICHLORIDE
PHOSPHORUS OXYCHLORIDE

FIGURE I
FLOW OF MATERIALS IN THE NON-FERTILIZER PHOSPHORUS CHEMICALS INDUSTRY

Ferrophosphorus, widely used in the metallurgical industries, is a direct by-product of the phosphorus production process, since most furnace-grade phosphate rock contains 2 to 6 percent iron oxide.

Over 87 percent of the elemental phosphorus is used to manufacture high-grade phosphoric acid by the furnace or "dry" process as opposed to the wet process which coverts phosphate rock directly into phosphoric acid. This lower-grade wet process acid is almost exclusively used in the fertilizer industry and is separately discussed in that report. The remainder of the elemental phosphorus is either marketed directly or converted to chemicals such as phosphorus pentoxide, phosphorus pentasulfide, phosphorus trichloride, and phosphorus oxychloride. These chemicals are chiefly used in synthesis in the organic chemicals industry.

Much of the furnace-grade phosphoric acid is directly marketed, largely to the food industry and to the high-grade fertilizer industry. Phosphoric acid is also used to manufacture two basic classes of phosphates: water-soluble phosphates used in detergents and for water treatment, typified by sodium tripolyphosphate, and water-insoluble phosphates which are used in animal feeds and in foods, typified by the calcium phosphates.

The processes involved in the non-fertilizer phosphorus chemicals industry are very briefly as follows:

Elemental phosphorus and ferrophosphorus are manufactured by the reduction of phosphate rock by coke in very large electric furnaces, using silica as a flux. Very large quantities of water are circulated for cooling the very hot equipment, for cooling and granulating the slag, and for condensing the phosphorus vapor from the furnace. Since water is both non-reactive and immiscible with liquid phosphorus, water is used extensively in direct contact with phosphorus for heat transfer, for materials transfer, for protection from the atmosphere, and for purification. This study is concerned with manufacturing operations subsequent to receiving washed phosphate ores at the phosphorus production facility. Ore benefication is commonly but not exclusively conducted at a separate off-site location. The huge waste load from benefication, 7500 kg of gangue per kkg of phosphorus eventually produced, warrants a separate study as a segment of the mining industry.

Phosphoric acid manufactured by the "dry" or furnace process consists of the burning of liquid phosphorus in air, the subsequent quenching and hydrolysis of the P_2O_5 vapor, and the collection of the phosphoric acid mists. The operation uses cooling water, and process water is consumed in making the aqueous acid. Solid wastes may be generated should a plant later purify the acid.

The manufacture of the anhydrous phosphorus chemicals (P_2O_5, P_2S_5, and PCl_3) is essentially by the direct union of phosphorus with the corresponding element. Phosphorus oxychloride, PCl_3, is manufactured from PCl_3 and air or from PCl_3, P_2O_5, and chlorine. Water use is limited to cooling water, to water for transferring elemental phosphorus, to scrubber water, and to wash water for reaction vessels and shipping containers.

Sodium tripolyphosphate is manufactured by the neutralization of phosphoric acid with the appropriate proportions of caustic soda and soda ash in mix tanks. The resulting mixture of mono- and di-sodium phosphates is dried and the crystals calcined to produce the tripolyphosphate.

The calcium phosphates are similarly made by the neutralization of phosphoric acid with lime. The amount and type of lime used and the amount of water in the process determine whether anhydrous monocalcium phosphate, monocalcium phosphate monohydrate, dicalcium phosphate dihydrate, or tricalcium phosphate is the final product. Table 2 lists production tonnages for these chemicals as reported by the U.S. Bureau of Census. As seen from this table the industry is relatively small in relation to numbers of plants.

Table 3 lists the current selling prices of the chemicals within this industry. Table 4 lists the producers of phosphate products.

TABLE 2. U.S. Production of Phosphates

Chemicals	Metric Tons	Short Tons	Number of Plants
Phosphorus	495,000	545,000	10
Ferrophosphorus	110,000*	121,000*	
Phosphoric Acid (Furnace Process)	1,640,000**	1,810,000**	25
Phosphorus Pentoxide	(withheld)	(withheld)	(withheld)
Phosphorus Pentasulfide	54,000	59,000	5
Phosphorus Trichloride	50,000	55,000	4
Phosphorus Oxychloride	28,000	31,000	4
Sodium Tripolyphosphate	945,000	1,040,000	17
Calcium Phosphates	536,000	592,000	7

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*Independently estimated.(2)

**Estimated as 87 percent of phosphorus consumption, using 90 percent conversion, and stated as acid of 54 percent P_2O_5. The total production of phosphoric acid both wet and dry was 5,650,000 kkg (6,240,000 short tons).

TABLE 3. Current Selling Prices of Phosphorus Chemicals
Source: Chemical Marketing Reporter, June 25, 1973

CHEMICAL	GRADE	SELLING PRICE	
		$/Metric Ton	$/Short Ton
White Phosphorus		419	380
Phosphoric Acid (Furnace)	75% Commercial & Feed	164	149
	80% Commercial & Feed	176	160
	85% National Formulary	194	176
Phosphorus Pentoxide		441	400
Phosphorus Pentasulfide		299	271
Phosphorus Trichloride		292	265
Phosphorus Oxychloride		270	245
Sodium Tripolyphosphate	Technical	179	162
	Food	270	245
Monocalcium Phosphate	Anhydrous Food	314	285
Dicalcium Phosphate	U.S.P Food	286	259
	Feed	82	74
Tricalcium Phosphate	NF Precip.	315	286

TABLE 4

Producers of Phosphate Products

	Phosphorus	Phosphorous Pentoxide	Phosphorous Trichloride	Phosphorous Oxychloride	Phosphorous Pentasulfide	Furnace Acid	Sodium Tripolyphosphate	Feedstock Dicalcium Phosphate	Technical Calcium Phosphate
Holmes Company	0								
FMC Corporation	0		0	0		0	0		
Mobil Corporation	0		0			0	0		
Monsanto Company	0		0	0	0	0	0		0
Occidental Petroleum Corp.	0	0	0	0	0	0	0	0	
Stauffer Chemical	0	0	0	0	0	0	0		0
TVA	0					0			
Olin Corporation							0		
Goodpasture, Inc.						0			
American Cyanamid Co.								0	
Borden, Inc.								0	
Eastman Kodak Co.									0
Farmland Industries								0	
Int'l. Minerals & Chemical Corp.								0	
Knox Gelatine, Inc									0
Richardson-Merrell, Inc.									0

DETAILED PROCESS DESCRIPTIONS

The following is a description of each process in this industry. Process flow diagrams are included. In generating the following process descriptions, emphasis has been placed on process features which generate aqueous wastes. The details of the waste stream character, however, have been left for discussion in Section V.

Much of the process data in this section were acquired by discussions with industry personnel and by observation of existing facilities. A large body of data also exists in the published literature, and was used extensively in the following discussion. Of particular usefulness were the publications of Beveridge and Hill;(4) Barber,(5,6) Barber and Farr;(7) LeMay and Metcalf(8) of The Tennessee Valley Authority, which supplied very specific operating details of TVA's facilities; Ellwood;(9) and Bryant, Holloway and Silber(10) of the Mobil Chemical Company. Standard reference books such as Faith, Keyes and Clark,(11) Kirk and Othmer,(12) and Shreve,(13) were also useful.

THE PHOSPHORUS PRODUCTION SEGMENT

Phosphorus is manufactured by the reduction of mined phosphate rock by coke in an electric furnace, with silica used as a flux. Slaq, ferrophosphorus (from iron in the phosphate rock), and carbon monoxide are reaction by-products. The simplified overall reaction may be written:

$$2Ca_3(PO_4)_2 + 10\ C + 6SiO_2 \xrightarrow{1250\ -\ 1500°C} P_4 + 10\ CO + 6CaSiO_3.$$

A typical material balance for the process is:

Raw Materials		Products	
Phosphate Rock	10.0 kkg	Phosphorus	1.0 kkg
Silica	1.5	Ferrophosphorus	0.3
Coke	1.5	Slag	8.9
		Carbon Monoxide	2.8
Total	13.0 kkg	Total	13.0 kkg

The electrical power consumption is approximately 15,400 KWH/kkg (14,000 KWH/ton) of phosphorus produced; part of this supplies the endothermic heat of reaction of 6,200 KWH/kkg of P_4.

The standard process, as pictured in Figure 2, consists of three basic parts: phosphate rock preparation, smelting in the electric furnace, and recovery of phosphorus.

Phosphate rock ores are first blended so that the furnace feed is of uniform composition. The silica composition is important since the overall furnace feed must have a SiO_2/CaO ratio close

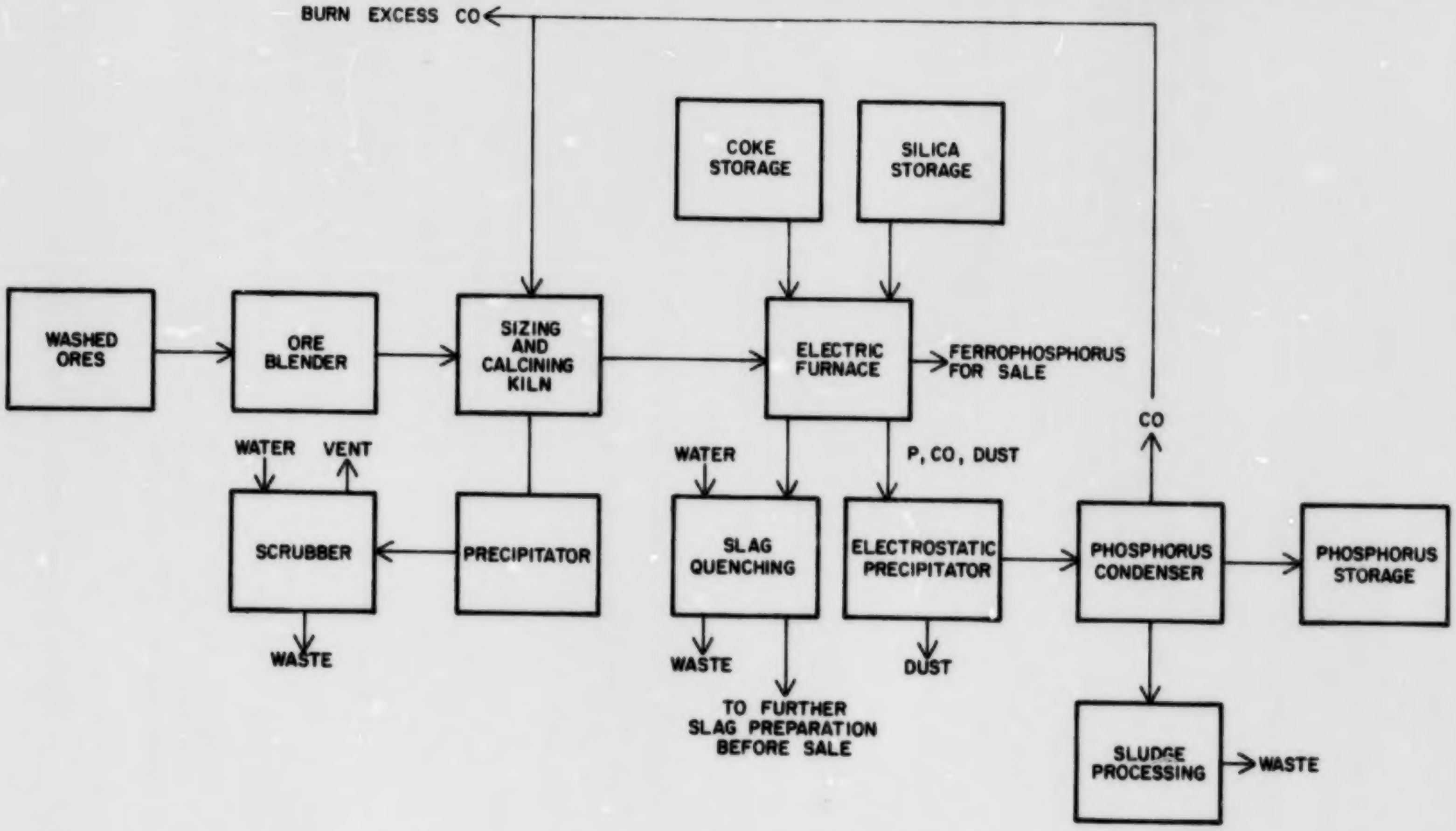

BURN EXCESS CO
COKE STORAGE
SILICA STORAGE
WASHED ORES
ORE BLENDER
SIZING AND CALCINING KILN
ELECTRIC FURNACE
FERROPHOSPHORUS FOR SALE
CO
WATER
VENT
P, CO, DUST
WATER
SCRUBBER
PRECIPITATOR
SLAG QUENCHING
ELECTROSTATIC PRECIPITATOR
PHOSPHORUS CONDENSER
PHOSPHORUS STORAGE
WASTE
WASTE
TO FURTHER SLAG PREPARATION BEFORE SALE
DUST
SLUDGE PROCESSING
WASTE

FIGURE 2
STANDARD PHOSPHORUS PROCESS FLOW DIAGRAM

to the eutectic composition for desired slag flow properties. The blended phosphate rock is carefully pretreated by drying, by agglomerating the particles, and by heat treatment.

After the raw phosphate rock is dried, sizing or agglomeration is accomplished by pelletizing, briquetting, flaking, or "nodulizing," and pre-formed agglomerates are then calcined in a rotary kiln. The nodulizing operation performs simultaneous agglomeration and calcining by heating the rock to its incipient fusion point, with subsequent crushing, sizing, and recycling of fines. Sizing promotes the even distribution of gas flow within the furnace and results in more efficient heat transfer and lower total energy costs. The size of the furnaces has dramatically increased in recent years, accentuating the needs for stoichiometric balance and thermal homogeneity within the charge (or "burden"). Heat treatment or calcining of the feed increases the strength and hardness of the particles, preventing large quantities of fines from being formed by attrition.

The calcining, at 1000 to 1400°C, also liberates water of hydration, organics, carbon dioxide, and fluorine at a much lower energy cost than would be required in the subsequent electric furnace operation. Since 25 percent of the manufacturing costs of phosphorus are for electric power, considerable effort is made to conserve this power. Moreover, by-product carbon monoxide from the smelting operation is available as a source of auxiliary energy.

The sizing and calcining operations are sources of dust and of fluorine fumes. The dust may be electrostatically precipitated, and the gases are scrubbed with water, removing fluorine as HF and H_2SiF_6. The dry dusts collected are normally recycled to the nodulizing operation.

The burden of treated phosphate rock, coke, and sand is charged to the furnace by incrementally adding weighed quantities of each of the three materials to a common belt conveyor. The furnace itself has a carbon crucible, carbon-lined steel sidewalls and a two-foot-thick self-supporting cast concrete roof. In an effort to eliminate periodic roof replacement due to excessive cracking of the concrete, some newer furnaces have anti-magnetic (to avoid induction heating) stainless steel roof structures. Penetrations in the furnace are for feed chutes, for carbon electrodes, for tap holes, for slag (upper liquid layer), for ferrophosphorus (lower liquid layer), and for exhaust gases.

Electric furnaces for phosphorus production have been dramatically increasing in size to achieve operating economies:

Year	Size of Largest Furnace in Operation Megawatts	kkg/Year	Tons/Year
1950	25	13,600	15,000
1960	50	27,200	30,000
1970	65	36,300	40,000

The smallest furnaces produce 9,100 kkg (10,000 tons) of phosphorus per year.

An appreciation of the physical size may be attained from the fact that the largest carbon electrodes used are 1.5 to 1.8 meters (5 to 6 feet) in diameter and carry 50,000 amperes each.

The furnace is extensively water-cooled. Cooling water is used for the electrical transformer, for the furnace shell, for the crucible bottom, for the fume hood, for the tapholes, and for electrode joints. Newer furnaces use telescoping water seals on furnace electrodes; and for TVA-type furnaces with rotating crucibles a water seal is provided between the crucible and the stationary roof.

The 2 to 6 percent Fe_2O_3 in the furnace-grade phosphate rock is reduced, with the iron recovered as the ferrophosphorus alloy:

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO$$
$$8Fe + P_4 \rightarrow 4Fe_2P$$

The ferrophosphorus typically contains 59 percent iron and 22 percent phosphorus and is marketed for the production of phosphorus alloys. The vanadium content of ferrophosphorus adds to its value. Should the marketplace be favorable for ferrophosphorus, iron slugs can be added to the furnace charge. Alternately, should a soft market for ferrophosphorus occur, the ferrophosphorus can be converted into high-grade metallurgical iron and fertilizer phosphates. An important degree of freedom is in the ore blending operation, where ores of appropriate iron content may be selected depending on the ferrophosphorus market.

Slag and ferrophosphorus are tapped periodically. The air cooled ferrophosphorus is sold in lumps to the metallurgical industry; no water is involved either in ferrophosphorus cooling or in subsequent product preparation.

The slag may typically contain 38 percent SiO_2 and 48 percent CaO, and also contain considerable quantities (depending of course on the ore composition) of Al_2O_3, CaF_2, K_2O, and MgO, with traces of uranium and other heavy metals. The slag may be air-cooled, but water quenching is more typical. High-density slag is produced by adding water to molten slag in a pit, and by subsequently breaking it up and shipping aggregate for railroad bed or roadbed construction. Alternately, a high-velocity water stream may be used on the molten slag to produce a low density expanded or granulated slag which has a market in concrete formulation. In either event, some of the fluorides from the slag are captured by the quenching water, either as soluble fluorides or as suspended solids.

There are numerous sources of fumes from the furnace operation. The feeding operation is a source of dust, and fumes are emitted from the electrode penetrations and from tapping. These fumes, consisting of dust, phosphorus vapor (which is immediately oxidized to phosphorus pentoxide), and carbon monoxide are often collected and scrubbed.

The hot furnace gases, consisting of 90 percent CO and 10 percent P_4, pass through an electrostatic precipitator to remove the dust before phosphorus condensation. Unless this dust was removed, it would later be emulsified by liquid phosphorus and water, forming large amounts of "phosphorus mud" or sludge which would be difficult and costly to handle.

The precipitator is a most unusual piece of equipment. In the phosphorus process, the precipitator is in the main process stream, as opposed to its usual application in an exhaust stream. Because of this, it is gas-tight (especially since any air would cause phosphorus combustion). It operates at very high temperatures with the inlet gas approaching 540°C (1000°F), and its surfaces must be maintained hot to prevent phosphorus condensation (the dew point of phosphorus is 180°C (356°F)). The precipitator is typically a tube bundle, with the gas passing through the tubes and with a high-voltage wire along the axis of each tube. Both the wire and the tube are mechanically shaken to release the dust into a hopper. In some installations, the dust is slurried in water and pumped to a settling pond, and the solids are recycled to the raw feed for recovery of phosphate values (the clarified pond effluent is reused in the slurrying operation).

The high-voltage wires may be insulated from the shell with an oil seal. Contaminated oil is periodically replaced with fresh oil. Alternatively, a quartz seal may be used. The entire unit is heated either electrically or by an inert gas jacket of by-product carbon monoxide combustion gases.

Downstream of the precipitator, the phosphorus is condensed by direct impingement of a hot water spray, which is sometimes augmented by heat-transfer through water-cooled condenser walls. The liquid phosphorus (freezing point 44°C (111°F)) drains into a water sump, where the water maintains a seal from the atmosphere. This water is partially neutralized by addition of ammonia or caustic to minimize corrosion, and then is recirculated from the sump to the phosphorus condenser.

Liquid phosphorus is stored in steam-heated tanks under a water blanket and is transferred into tank cars by pumping or by hot water displacement. The tank cars also have a protective blanket of water and are equipped with steam coils for remelting at the destination.

Despite very high precipitator removal efficiencies, enough dust reaches the condensers to form some phosphorus mud, which is typically 10 percent dust, 30 percent water, and 60 percent phosphorus.

The condenser exhaust gases are mainly carbon monoxide, which is either burned in a flare or used for heating elsewhere in the plant.

THE PHOSPHORUS-CONSUMING SEGMENT

Phosphoric Acid (Dry Process)

Phosphoric acid is made from elemental phosphorus in the "dry" process, as opposed to the acidulation of phosphate rock in the "wet" process. The wet process is discussed in a separate report dealing with the fertilizer industry. Furnace acid, as dry-process phosphoric acid is called, is relatively pure compared to wet-process acid, as Table 5 indicates. Consequently, the furnace acid is primarily used for preparing foodstuffs, detergents, and other high-grade products, while wet acid is primarily used for preparing fertilizers and animal feed supplements.

TABLE 5. Impurities in Phosphoric Acid (54% P_2O_5)

	Wet Process Acid	Furnace Acid
F, wt %	0.6 - 1.0	0.007
SO_3, wt %	2.7	0.003
Al_2O_3, wt %	0.9	0.001
Fe_2O_3, wt %	1.2	0.0007
Water insolubles, wt %	0.8	
Total Impurities, wt %	6.2 - 6.6	0.012
Density, kg/l (lb/gal) @ 27°C (80°F)	1.72 (14.3)	1.57 (13.1)
Viscosity, cp @ 27°C (80°F)	85	18
Color	Black	Colorless

In the standard dry process illustrated in Figure 3, liquid phosphorus is burned in air, the resulting gaseous phosphorus pentoxide is absorbed and hydrated in a spray of water, and the mist is collected with an electrostatic precipitator.

The standard reaction may be written:

$$P_4 + 5O_2 \rightarrow 2P_2O_5 + 6H_2O \rightarrow 4H_3PO_4$$

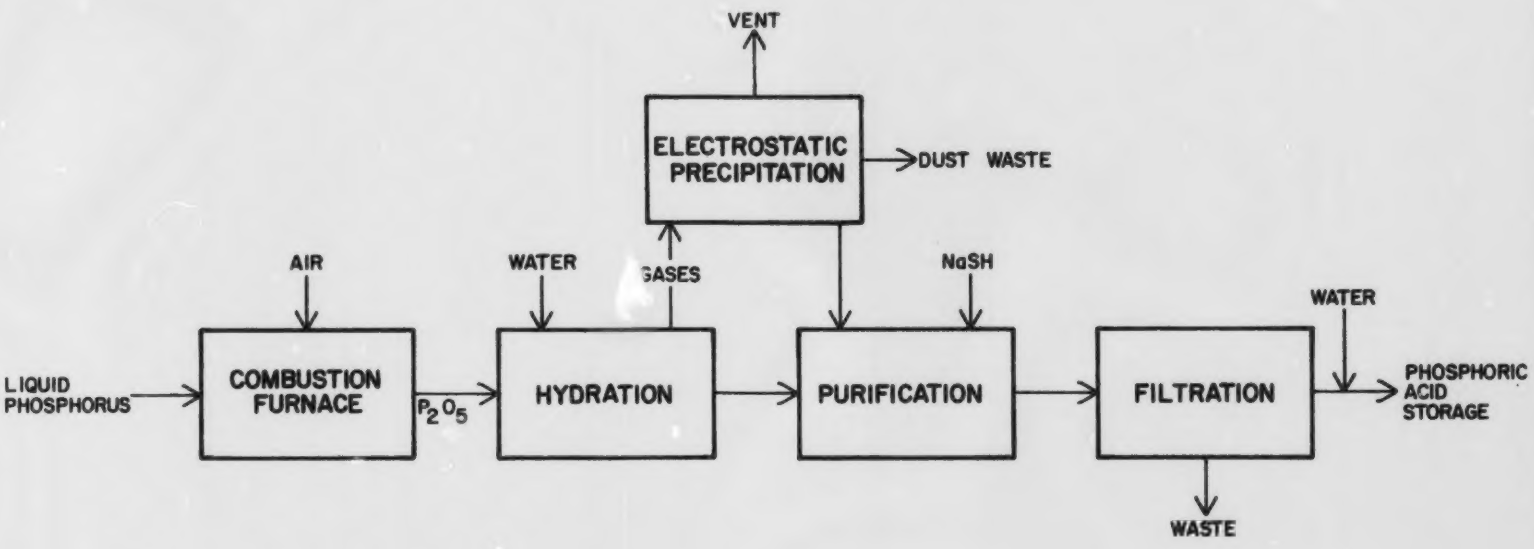

VENT
ELECTROSTATIC PRECIPITATION
DUST WASTE
AIR
WATER
GASES
NaSH
WATER
LIQUID PHOSPHORUS
COMBUSTION FURNACE
P_2O_5
HYDRATION
PURIFICATION
FILTRATION
PHOSPHORIC ACID STORAGE
WASTE

FIGURE 3
STANDARD PHOSPHORIC ACID FLOW DIAGRAM (DRY PROCESS)

Liquid phosphorus is stored under water in tanks heated with steam coils (the freezing point of phosphorus is 44°C (111°F)). The phosphorus may be fed to the burner by hot-water displacement in a feed tank, or in a loop with a steam-heated displacement water tank and water pump. Alternately, the liquid phosphorus may be pumped directly.

There are variations in the design of the liquid phosphorus injector. Some producers achieve fine atomization using air in a dual-fluid injector (where the injection orifice can be large enough to prevent plugging). To prevent freezing of the phosphorus in upstream portions of the injector and yet to keep the injector tip cool, intricate use of both steam and cooling water has been simultaneously applied. Other designs have proved successful for phosphorus atomization, including the exploitation of extreme turbulence in a pre-combustion zone. Some form of temperature control is required, since red phosphorus formed at combustion temperatures much higher than 1650°C (3000°F) would color the resulting acid and would plug injector orifices.

In the combustion chamber, corrosion by P_2O_5 vapors and by hot phosphoric acid (formed from the moisture in the air) is countered by using a graphite lining. The steel shell of the combustion chamber is cooled by running water down its exterior surfaces. This mode of heat transfer is standard; pressurized cooling water is avoided since any leaks would result in premature hydration. Recent plants have been constructed with stainless steel combustion chambers.

The gas exiting from the combustion chamber is typically 540°C (1000°F), and is then hydrated with direct water sprays which also reduce the temperature to 120°C (250°F) or less.

A variation of the standard process, illustrated in Figure 4, uses dilute acid for hydration instead of water. In this case, the make-up water is added in the vapor-liquid separation step. The rationale is that P_2O_5 vapor is absorbed more easily as the concentration of absorbing acid is increased. Another deviation from the standard process, also shown in Figure 4, is the use of a high-pressure-drop venturi scrubber to complete the somewhat difficult hydration, and a screen-type demister and separation tower instead of an electrostatic precipitator to free the tail gases of the persistent acid mist.

When an electrostatic precipitator is used for collection of the phosphoric acid mist, the corrosivity requires the use of carbon tubes and stainless steel high-voltage wires. Those plants using a high-pressure-drop venturi scrubber and a screen-type demister with a separation tower are of stainless steel construction. Where dilute phosphoric acid is used in the hydrator, the make-up water is added in the separation tower. Regardless of process variation, phosphoric acid is made with consumption of water; no aqueous waste streams are generated by the process.

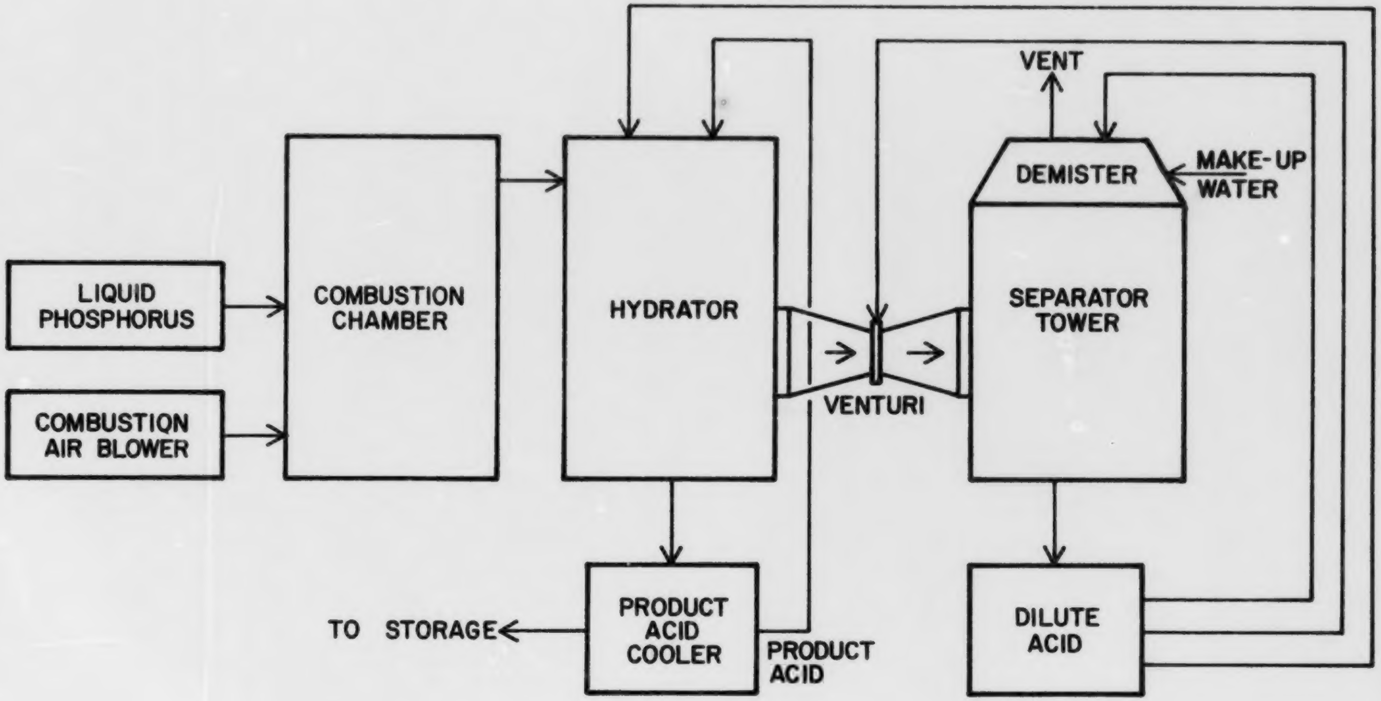

LIQUID PHOSPHORUS
COMBUSTION AIR BLOWER
COMBUSTION CHAMBER
HYDRATOR
VENTURI
VENT
DEMISTER
MAKE-UP WATER
SEPARATOR TOWER
PRODUCT ACID COOLER
PRODUCT ACID
TO STORAGE
DILUTE ACID

FIGURE 4
VARIATIONS OF PHOSPHORIC ACID (DRY) PROCESS

The product acid is pure, but for the manufacture of food grade acid, traces of arsenic must be removed. Arsenic occurs naturally with phosphorus in the ore (they are both Group V-A elements) at a level of about 0.075 kg of arsenic per kkg of phosphorus (0.15 lb/ton). The arsenic is quantitatively carried through into the acid and is commonly removed by treatment with a soluble sulfide followed by filtration of the insoluble arsenic sulfide.

Phosphorus Pentoxide

The manufacture of solid anhydrous phosphorus pentoxide is similar to the first stages of phosphoric acid manufacture. Liquid phosphorus is burned in an excess of air:

$$P_4(l) + 5O_2 \rightarrow 2P_2O_5(s)$$

Figure 5 is a flow diagram for a standard phosphorus pentoxide manufacturing facility. A significant difference between the two processes is that in the anhydrous phosphorus pentoxide process the air is dried to an extremely low dew point, since any moisture results in a lumpy and agglomerated product not suited for its uses as a reactive drying agent and as a reactive condensing agent in organic synthesis. Typically, the ambient air is filtered, then refrigerated to achieve a dew point of -18 to -7°C (0 to 20°F), and then dried to a dew point of -46°C (-50°F) with silica gel.

After reaction of liquid phosphorus with excess dried air in the combustion chamber, the P_2O_5 vapor is condensed to a solid in a "barn," which is a room-like structure. Some installations use a more conventional tower for condensation. Both the combustion chamber and the barn (or tower) are cooled by an external flow of water down the surfaces; pressurized cooling water is avoided since any leaks would result in lumpy, unacceptable product.

Condensed phosphorus pentoxide solid is mechanically scraped from the walls using moving chains, and is discharged from the bottom of the barn or tower with a screw conveyor. The gases are vented to the atmosphere through a tail gas water seal which absorbs any P_2O_5 vapor or solid carry-over. There is usually continuous water addition and overflow for the tail gas seal.

The product particle size is sensitive to the rate of cooling and condensation in the barn or tower. In a barn, the external surface-to-volume ratio is small, a relatively high temperature is maintained in the condensing unit, and rather large crystals may grow. In a tower, heat transfer is more rapid, and the product is very finely divided. One installation uses two towers in series; the first has much higher heat transfer rates and results in a coarser product than the second, and the products from the two towers are separately packaged.

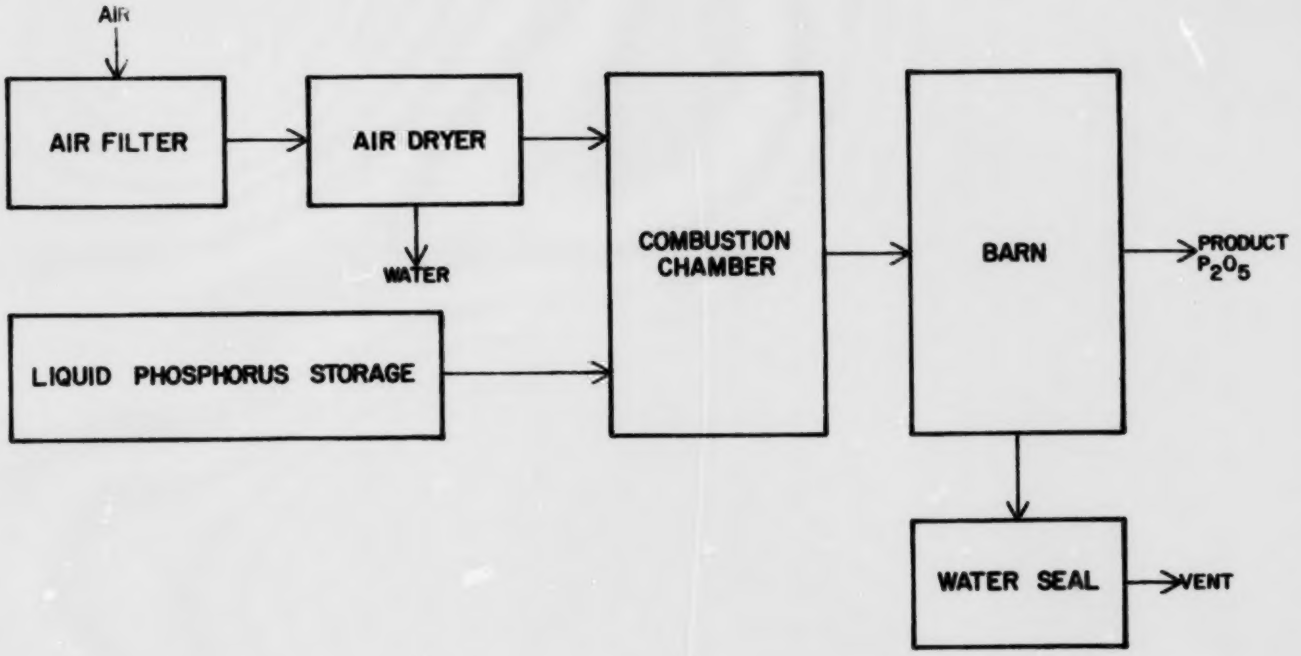

AIR
AIR FILTER
AIR DRYER
WATER
LIQUID PHOSPHORUS STORAGE
COMBUSTION CHAMBER
BARN
PRODUCT P_2O_5
WATER SEAL
VENT

FIGURE 5
PHOSPHORUS PENTOXIDE MANUFACTURE FLOW DIAGRAM

Phosphorus Pentasulfide

The standard process for the manufacture of phosphorus pentasulfide, shown in Figure 6, is by direct union of the elements, both in liquid form:

$$P_4(l) + 10S(l) \rightarrow 2P_2S_5(l)$$

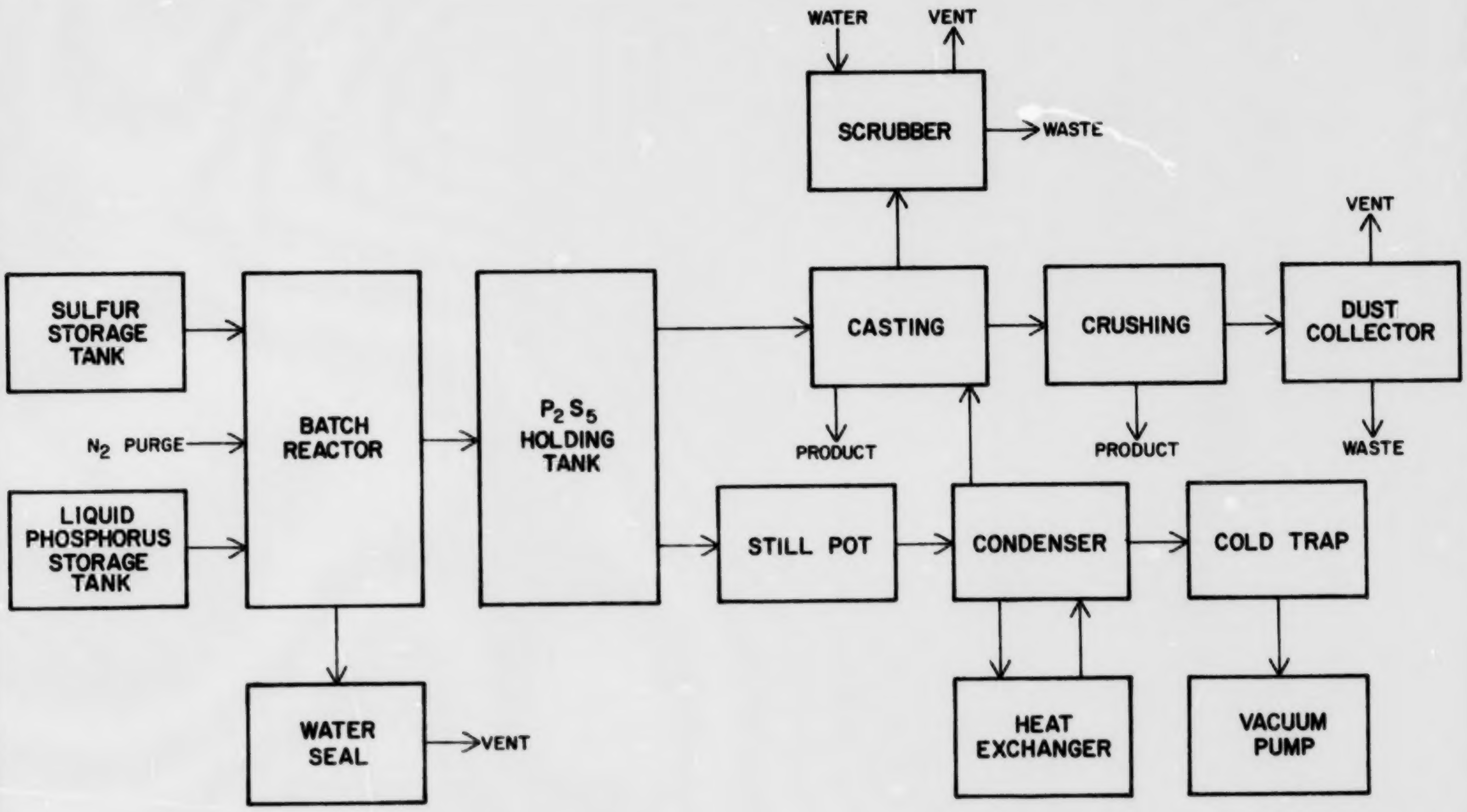
The largest use of phosphorus pentasulfide is for the manufacture of lubricating oil additives.

Liquid sulfur (melting point 113°C (230°F)) is transferred from a steam-heated storage tank using submerged pumps, and liquid phosphorus (melting point 44°C (111°F)) is transferred by hot water displacement. The highly exothermic reaction is usually carried out as a batch operation in stirred cast iron pots. A "heel" of molten P_2S_5 (melting point 282°C (540°F)) from the previous batch is used to absorb the initial heat of reaction. Liquid phosphorus and liquid sulfur are incrementally added. Since the reactants and the product are extremely flammable at the reaction temperature, the reactor is continuously purged with nitrogen. A water seal is used in the vent line.

The batches from multiple reactors are forced into an electrically heated (300°C (570°F)) P_2S_5 holding tank by nitrogen pressure. Some of the P_2S_5 is converted directly into product, while the rest is purified. Liquid P_2S_5 from the holding tank that is to be sold is cast directly into drums or into cones. When the molten product contacts air during casting, it ignites, and fumes of P_2O_5 and SO_2 are generated. A fume hood and water scrubber are used. The cones, after cooling, are crushed and packaged; solid P_2S_5 does not auto-ignite in air. The dust from the crushing operation is removed in a dry separation system such as a cyclone.

The liquid P_2S_5 that is to be purified may be vacuum distilled (normal boiling point is 515°C (960°F)) in a continuous system. The condenser is cooled by a high-temperature heat transfer fluid, which in turn is cooled in a water-cooled heat exchanger. The condenser is operated between the melting and boiling points of the product. Molten purified P_2S_5 is then cast and crushed, sharing the fume scrubber and dust collection systems with the impure product operation.

An alternate mode of purification is the washing of crushed P_2S_5 with carbon disulfide, in which the by-products phosphorus sesquisulfide (P_4S_3) and free sulfur are soluble.



WATER
VENT
SCRUBBER
WASTE
VENT
SULFUR STORAGE TANK
BATCH REACTOR
P_2S_5 HOLDING TANK
CASTING
CRUSHING
DUST COLLECTOR
N_2 PURGE
PRODUCT
PRODUCT
WASTE
LIQUID PHOSPHORUS STORAGE TANK
STILL POT
CONDENSER
COLD TRAP
WATER SEAL
VENT
HEAT EXCHANGER
VACUUM PUMP

FIGURE 6

PHOSPHORUS PENTASULFIDE MANUFACTURE FLOW DIAGRAM

Phosphorus Trichloride

Phosphorus trichloride, used extensively in organic synthesis, is manufactured directly from the elements:

$$P_4(l) + 6Cl_2(g) \rightarrow 4PCl_3(l)$$

The standard process is shown in Figure 7. Liquid phosphorus is charged to a jacketed batch reactor. Chlorine is bubbled through the charge, and phosphorus trichloride product (melting point -112°C (-173°F)), boiling point 74°C (165°F), is refluxed until all the phosphorus is consumed. Some cooling water is used in the reactor jacket since the formation of PCl_3 is exothermic. Care is taken to avoid an excess of chlorine; otherwise, phosphorus pentachloride is formed.

When the reaction is complete, the cooling water to the reflux condenser is turned off, steam is supplied to the reactor jacket, and the product of the batch distillation is condensed and collected.

A water scrubber collects hydrochloric acid and phosphorous acid, the hydrolysis products of PCl_3 vapors:

$$PCl_3 + 3H_2O \rightarrow 3HCl + H_3PO_3$$

The vapor pressure of the product is sufficiently high so that the fumes from transferring the product into shipping containers are also collected and scrubbed.

In a variation of the standard process, the reaction is conducted semi-continuously instead of batch-wise. The reflux condenser of Figure 7 is tailored so that only a small fraction of the PCl_3 is withdrawn as product; the larger fraction of condensed PCl_3 returns to the reactor and serves as the working fluid and heat sink for the reaction, since elemental phosphorus is somewhat soluble in PCl_3. Gaseous chlorine is added continuously, and liquid phosphorus is added incrementally.

No provision is generally made for continuous or frequent withdrawal of residue from the reactor either in the batch process or in the semi-continuous process. Instead, the residue is permitted to accumulate, and the reactor is shut down for cleanout infrequently.

Phosphorus trichloride is corrosive and is often shipped in returnable nickel drums. Before use, these drums are thoroughly washed with water and steam cleaned. Some recent use has been made of non-returnable epoxy-lined steel drums.

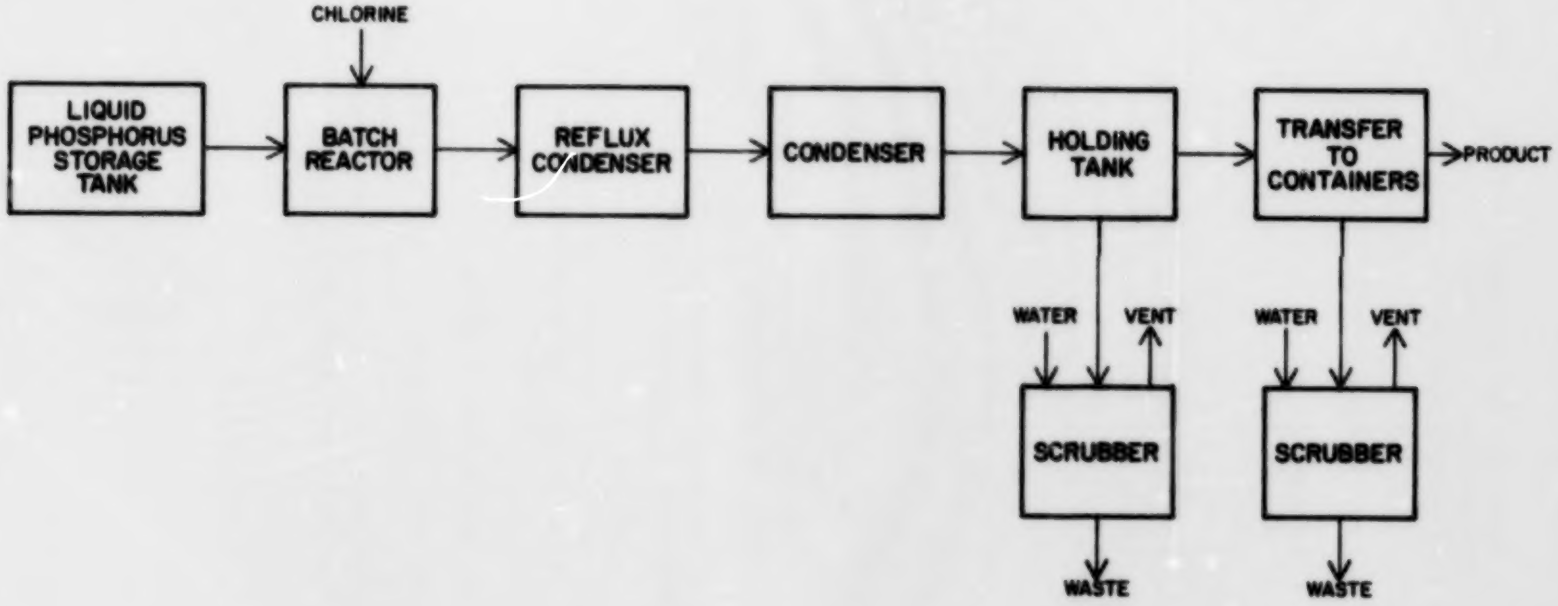

CHLORINE
LIQUID PHOSPHORUS STORAGE TANK
BATCH REACTOR
REFLUX CONDENSER
CONDENSER
HOLDING TANK
TRANSFER TO CONTAINERS
PRODUCT
WATER
VENT
SCRUBBER
WASTE
WATER
VENT
SCRUBBER
WASTE

FIGURE 7
PHOSPHORUS TRICHLORIDE MANUFACTURE FLOW DIAGRAM

Phosphorus Oxychloride

Phosphorus oxychloride, used in the preparation of organic phosphate esters and pharmaceuticals, is manufactured by the reaction of liquid phosphorus trichloride, chlorine, and solid phosphorus pentoxide:

$$3\ PCl_3(l) + 3\ Cl_2(g) + P_2O_5(s) \rightarrow 5\ POCl_3\ (l)$$

The standard process, illustrated in Figure 8, is carried out in a batch reactor and still which are very similar to the standard phosphorus trichloride equipment. Liquid phosphorus trichloride is charged to the reactor, solid phosphorus pentoxide is added, and chlorine is bubbled through the mixture while the PCl_3 (boiling point 74°C (165°F)) and later the $POCl_3$ (boiling point 105°C (221°F)) are refluxed. When the reaction is complete, steam is supplied to the reactor jacket, the water to the reflux condenser is shut off, and the product is distilled over and collected.

An alternative process for the manufacture of phosphorus oxychloride from phosphorus trichloride is also in commercial use. As is shown in Figure 9, dried air is used as the oxidant in a batch process. A water-cooled reflux condenser is used as in the standard process, except that a refrigerated condenser is added in series to ensure total reflux of the PCl_3 upstream of a water scrubber for the tail gas. The significant difference is that in the air-oxidation process a large quantity of non-condensible gas (nitrogen and excess oxygen) is involved.

Instead of a final distillation step, the product $POCl_3$ is filtered, with periodic changing of the cartridge filter elements.

Water scrubbers collect hydrochloric acid and phosphoric acid, the hydrolysis products of $POCl_3$ vapors, both from the reaction/distillation equipment and from transferring operations (for either process):

$$POCl_3 + 3H_2O \rightarrow 3HCl + H_3PO_4$$

Like phosphorus trichloride, phosphorus oxychloride is extremely corrosive and is shipped in returnable nickel drums. Before reuse, these drums are thoroughly washed with water and steam cleaned. Some recent use has been made of non-returnable epoxy lined steel drums.

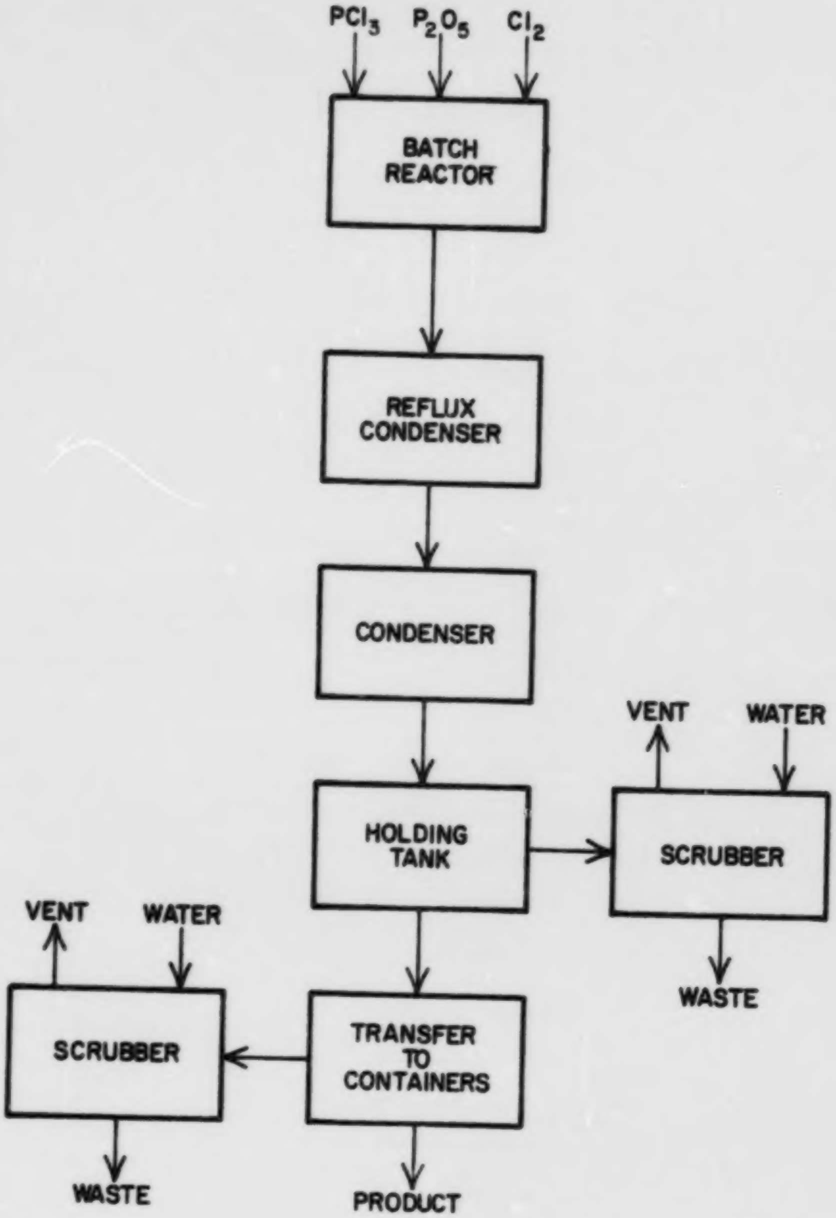

PCl_3
P_2O_5
Cl_2
BATCH REACTOR
REFLUX CONDENSER
CONDENSER
VENT
WATER
HOLDING TANK
SCRUBBER
WASTE
VENT
WATER
SCRUBBER
TRANSFER TO CONTAINERS
WASTE
PRODUCT

FIGURE 8
STANDARD PROCESS FOR
PHOSPHORUS OXYCHLORIDE MANUFACTURE

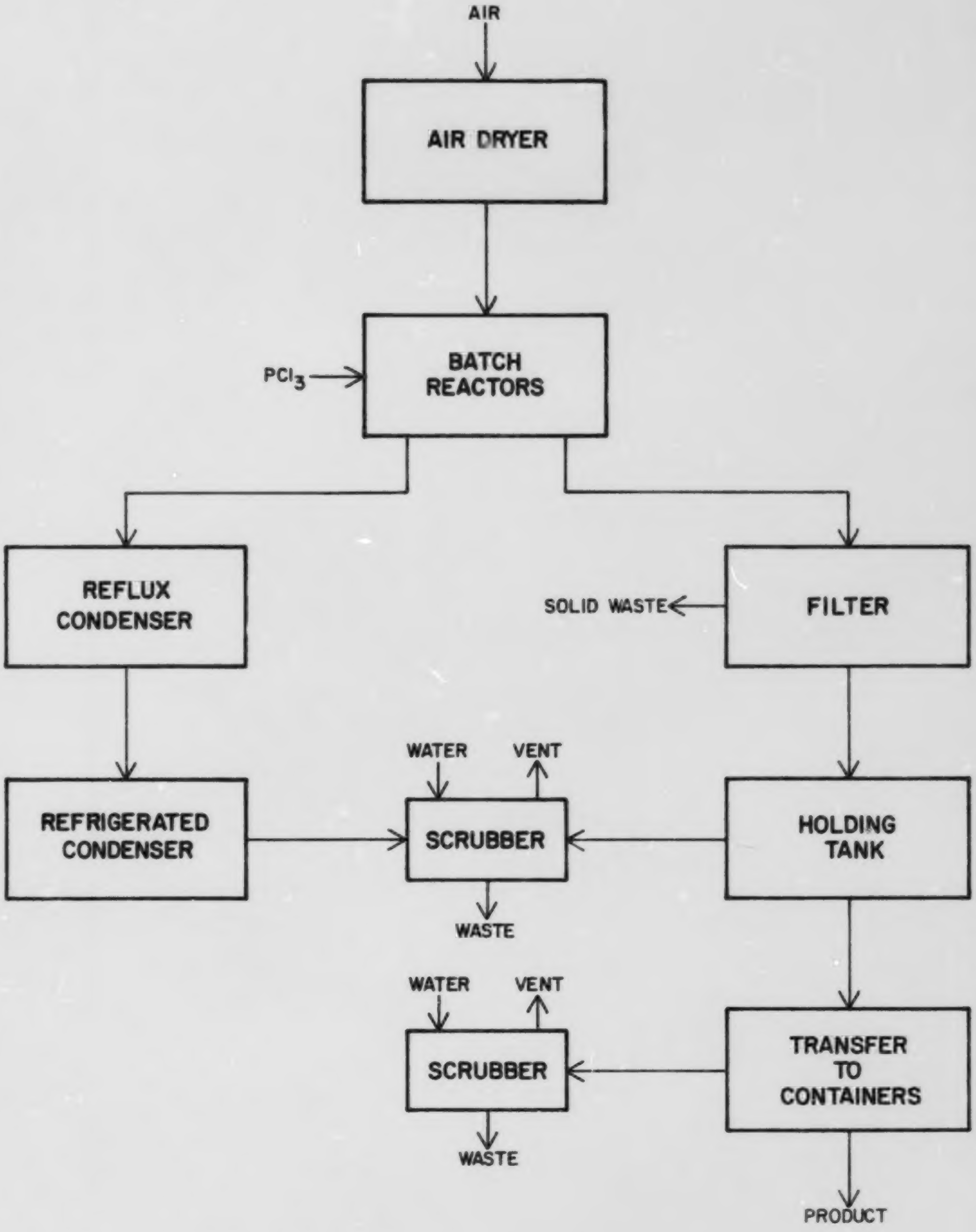

AIR
AIR DRYER
PCl3
BATCH REACTORS
REFLUX CONDENSER
FILTER
SOLID WASTE
REFRIGERATED CONDENSER
WATER
VENT
SCRUBBER
WASTE
HOLDING TANK
WATER
VENT
SCRUBBER
WASTE
TRANSFER TO CONTAINERS
PRODUCT

FIGURE 9
ALTERNATE PROCESS FOR
PHOSPHORUS OXYCHLORIDE MANUFACTURE

THE PHOSPHATE SEGMENT

Sodium Tripolyphosphate

Sodium tripolyphosphate is manufactured by the neutralization in mix tanks of phosphoric acid by soda ash or by caustic soda and soda ash, with the subsequent calcining of the dried mono- and di-sodium phosphate crystals. Figure 10 is a flow diagram of the standard process. The sodium tripolyphosphate product is widely used in detergents and in water-softening applications. In the neutralization step, the amount of raw material is measured and controlled to yield monosodium orthophosphate and disodium orthophosphate in a 1:2 mole ratio:

$$6H_3PO_4 + 5Na_2CO_3 \rightarrow 2NaH_2PO_4 + 4Na_2HPO_4 + 5H_2O + 5CO_2,$$

or

$$9H_3PO_4 + 5NaOH + 5Na_2CO_3 \rightarrow 3NaH_2PO_4 + 6Na_2HPO_4 + 10H_2O + 5CO_2$$

In either process variation, the final pH in the mix tank is very carefully adjusted by small additions of either phosphoric acid or caustic soda solution.

The mixture of sodium orthophosphates is spray dried or drum dried and the solids calcined to produce the sodium tripolyphosphate:

$$NaH_2PO_4 + 2\ Na_2HPO_4 \rightarrow Na_5P_3O_{10} + 2\ H_2O$$

The product is then slowly cooled or tempered to preserve the condensed form of the phosphates. If the product is chilled too rapidly, it will revert to a mixture of the meta- and polyphosphates:

$$Na_5P_3O_{10} \rightarrow Na_3PO_3 + Na_2P_2O_7$$

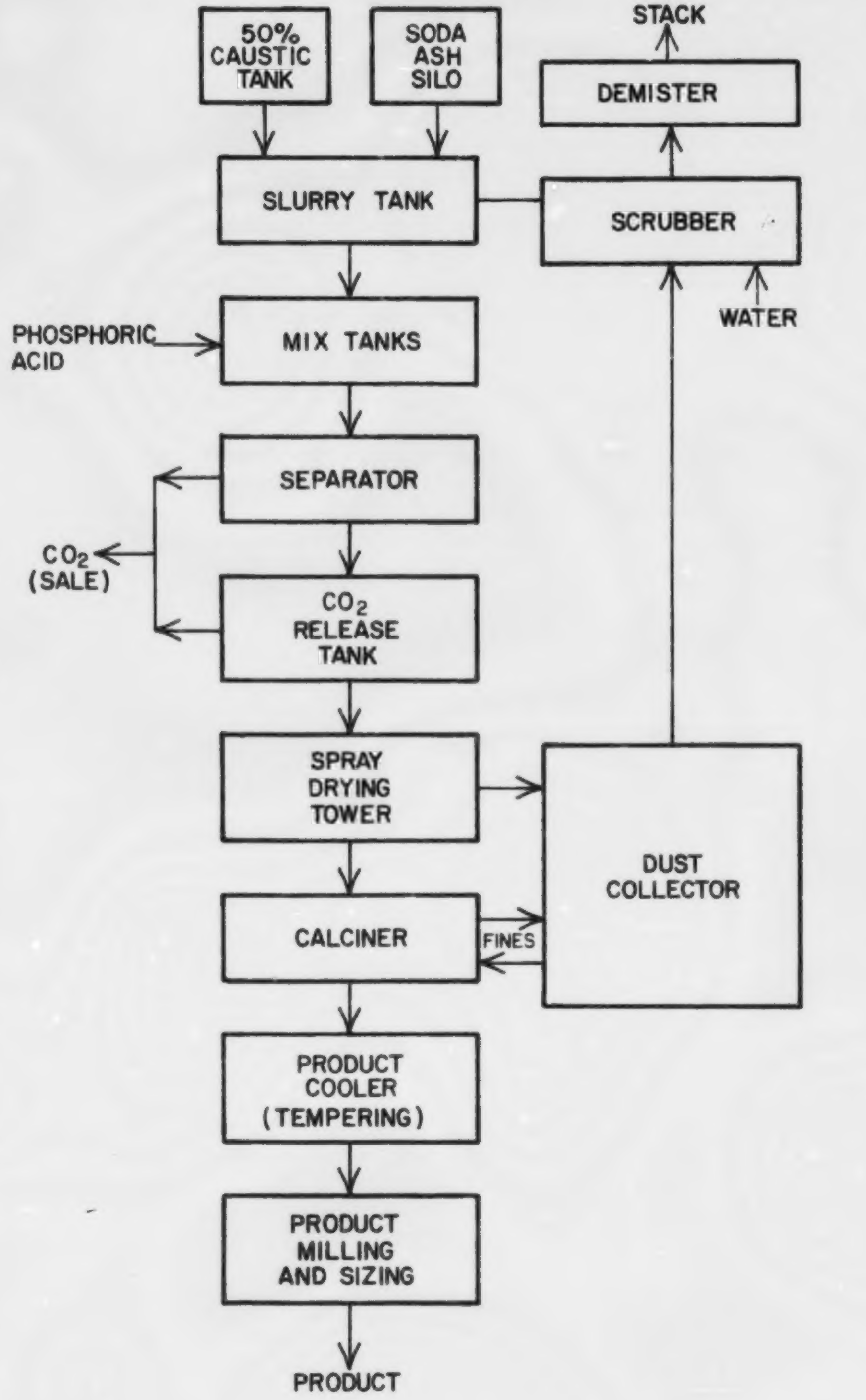

50% CAUSTIC TANK
SODA ASH SILO
STACK
DEMISTER
SLURRY TANK
SCRUBBER
WATER
PHOSPHORIC ACID
MIX TANKS
SEPARATOR
CO_2 (SALE)
CO_2 RELEASE TANK
SPRAY DRYING TOWER
DUST COLLECTOR
CALCINER
FINES
PRODUCT COOLER (TEMPERING)
PRODUCT MILLING AND SIZING
PRODUCT

FIGURE 10
STANDARD PROCESS FOR
SODIUM TRIPOLYPHOSPHATE MANUFACTURE

Calcium Phosphates

The non-fertilizer calcium phosphates are made by the neutralization of phosphoric acid with lime. Although the reactions are chemically similar, the processes for manufacturing the different calcium phosphates differ substantially from one another in the amount and type of lime used and the amount of process water used (See Figures 11 and 12).

Relatively pure, food grade monocalcium phosphate (MCP) is made in a stirred batch reactor from furnace acid and lime slurry:

$$2H_3PO_4 + Ca(OH)_2 \rightarrow Ca(H_2PO_4)_2 \cdot H_2O + H_2O$$

An excess of phosphoric acid maintained during the batch addition cycle inhibits the formation of dicalcium phosphate. A minimum quantity of process water is used. The heat of the reaction liberates some water as steam in the reactor, and the remaining water is evaporated in a vacuum dryer, a steam heated drum dryer, or a spray dryer. The anhydrous MCP is produced by using CaO (quicklime) and in carrying out the reaction at 140°C (310°F) so that water is driven off as it is produced.

Relatively pure food grade tricalcium phosphate (TCP) is made in a similar manner to MCP, except that an excess of lime slurry maintained during the batch addition cycle inhibits formation of dicalcium phosphate:

$$2H_3PO_4 + 3Ca(OH)_2 \rightarrow Ca_3(PO_4)_2 + 6H_2O$$

Like MCP, the TCP is dried to prevent excessive product temperatures.

Relatively pure, food grade dicalcium phosphate (DCP) is made in batch stirred reactors, but with much more process water than for either MCP or TCP:

$$H_3PO_4 + Ca(OH)_2 \rightarrow CaHPO_4 \cdot 2H_2O$$

The stoichiometry for DCP manufacture is critical; any excess H_3PO_4 during the batch addition cycle would result in some MCP and any excess $Ca(OH)_2$ would result in some TCP. The excess water in the DCP reactor is to ensure homogeneity so that the local stoichiometry is as balanced as the overall reactor stoichiometry.

As a result of the excess of water used, the reaction mixture is a pumpable slurry as opposed to the pasty consistency of MCP and TCP. This DCP is mechanically dewatered before drying.

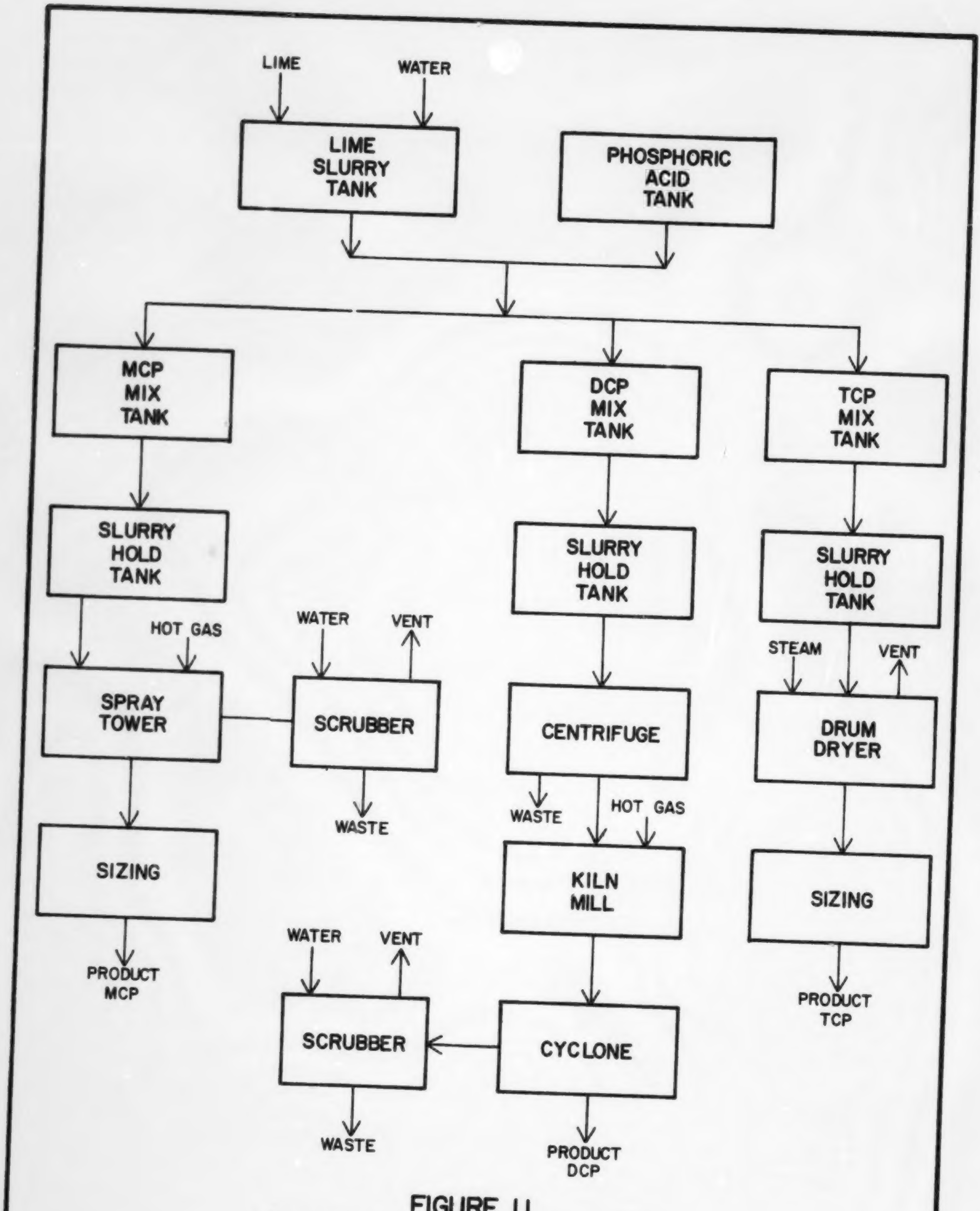

LIME
WATER
LIME SLURRY TANK
PHOSPHORIC ACID TANK
MCP MIX TANK
DCP MIX TANK
TCP MIX TANK
SLURRY HOLD TANK
SLURRY HOLD TANK
SLURRY HOLD TANK
HOT GAS
WATER
VENT
STEAM
VENT
SPRAY TOWER
SCRUBBER
CENTRIFUGE
DRUM DRYER
WASTE
WASTE
HOT GAS
SIZING
KILN MILL
SIZING
PRODUCT MCP
WATER
VENT
PRODUCT TCP
SCRUBBER
CYCLONE
WASTE
PRODUCT DCP

FIGURE 11
STANDARD PROCESS FOR
FOOD-GRADE CALCIUM PHOSPHATES

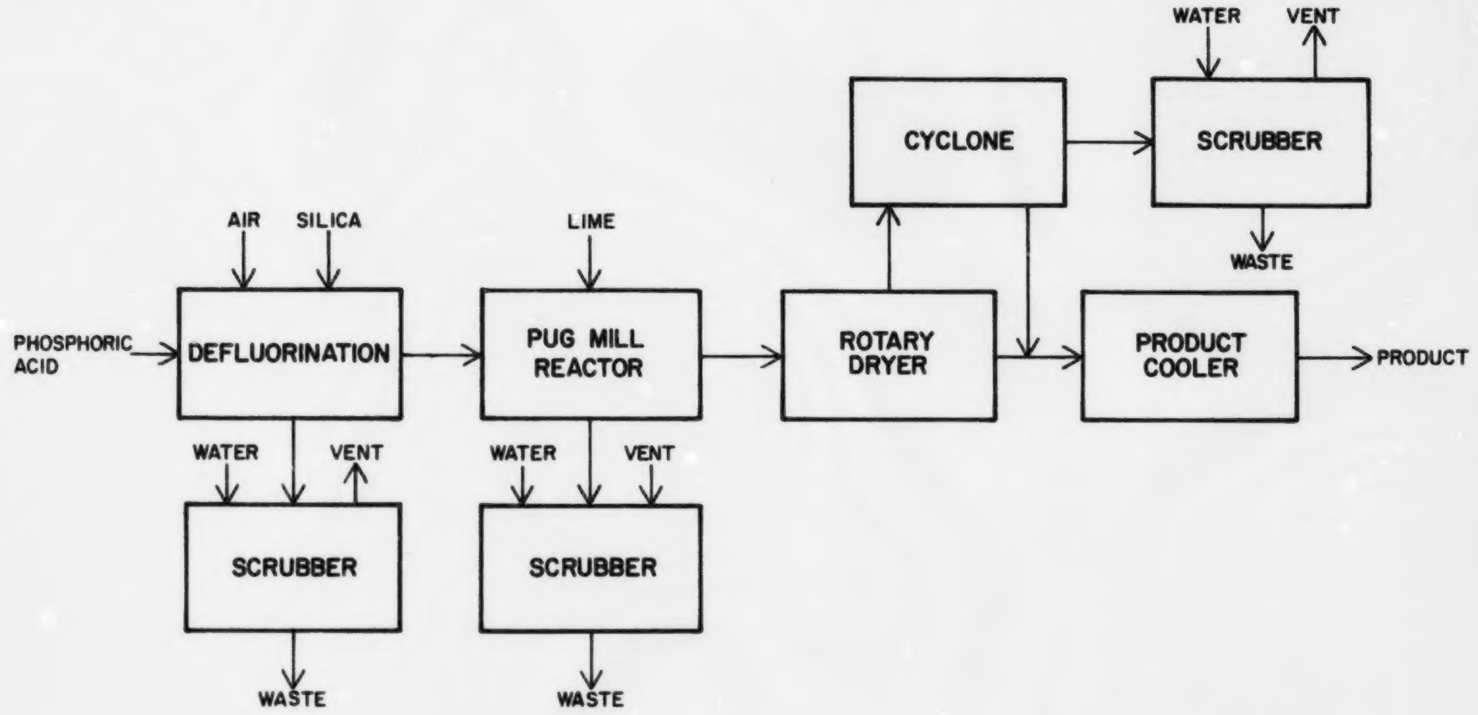

WATER
VENT
CYCLONE
SCRUBBER
AIR
SILICA
LIME
WASTE
PHOSPHORIC ACID
DEFLUORINATION
PUG MILL REACTOR
ROTARY DRYER
PRODUCT COOLER
PRODUCT
WATER
VENT
WATER
VENT
SCRUBBER
SCRUBBER
WASTE
WASTE

FIGURE 12
MANUFACTURE OF LIVESTOCK-FEED CALCIUM PHOSPHATE
FLOW DIAGRAM

Dicalcium phosphate (DCP) is also manufactured for livestock feed supplement use, with much lower specifications on product purity. Hence, the reaction can be conducted without excess water, since some MCP and/or TCP in the DCP product is perfectly tolerable. The pasty reaction product is normally dried in a rotary dryer. Powdered limestone, $CaCO_3$, may be used instead of lime. If quicklime is used, the drying step may be bypassed.

Another significant process difference is that non-food grade wet process phosphoric acid is normally used for this product. The DCP plants defluorinate the acid unless this step was accomplished by the acid producer. Wet process phosphoric acid contains approximately 1 percent fluoride in various forms. The defluorination consists of treating the heated acid with finely-divided silica and steaming or aerating, which liberates silicon tetrafluoride gas:

$$SiO_2 + 4HF \rightarrow SiF_4 + 2H_2O$$

Wet scrubbers then hydrolyze and collect this gas as fluosilicic acid and silicic acid:

$$3\ SiF_4 + 3H_2O \rightarrow 2H_2SiF_6 + H_2SiO_3$$

The hot defluorinated phosphoric acid is then charged to the reactor to make dicalcium phosphate.

SECTION IV

INDUSTRY CATEGORIZATION

INTRODUCTION

In developing effluent limitations guidelines and standards of performance for new sources for a given industry, a judgment must be made by the Environmental Protection Agency as to whether effluent limitations and standards are appropriate for different segments (subcategories) within the industry. The factors considered in determining whether such subcategories are justified for the phosphate category of point sources are:

wastes generated
treatability of waste waters
manufacturing process
raw materials
plant size and age
product
land availability
air pollution control equipment

WASTES GENERATED

Tables 7, 8, and 9 in section V show the raw waste loads for the phosphate category. Suspended solids and dissolved phosphates are common raw waste water constituents for phosphorus, food grade calcium phosphates, and feed grade calcium phosphates. Dissolved solids are present in concentrations significantly above background for all the chemicals studied. Elemental phosphorus can be a waste water constituent common to all of the phosphate manufacturing industry if the phossy transport water is not returned to the phosphorus producing plant. Sulfates, fluorides and alkalinity are constituents and parameters specific to phosphorus production. Furthermore, the amount of waste water (425,000 l/kkg of P_4) resulting from the production of phosphorus is several orders of magnitude greater than that generated from any of the other processes. The chemicals H_3PO_4, P_2O_5, P_2S_5, PCl_3, and $POCl_3$ commonly generate acidic wastes and phosphates.

TREATABILITY OF WASTE WATERS

Phosphorus production clearly stands alone on the basis of waste water treatability. The large amount of waste water produced (425,000 l/kkg P_4) presents special problems. It is commonly practiced within the industry to return phossy transport water to the phosphorus plant. Therefore, the problem of treating elemental phosphorus is only a phosphorus plant problem or can be so handled that it will be a problem unique to phosphorus plants.

The chemicals H_3PO_4, P_2O_5, P_2S_5, PCl_3, and $POCl_3$ present similar treatability problems in that acidic wastes are encountered. PCl_3 and $POCl_3$ present more difficult problems because the resultant chloride ions are difficult to remove.

The calcium phosphates involve similar treatment problems (suspended solids and phosphates). Defluorination of animal feed grade calcium phosphates will produce fluoride wastes, but the proposed treatment schemes will handle this waste constituent.

MANUFACTURING PROCESS

Manufacturing process is the principal factor used to determine subcategories. Phosphorus production is an ore reduction process involving large electric furnaces and large amounts of raw material and slag. Ferrophosphorus is a by-product in the phosphorus reaction and is always considered along with phosphorus when considering effluent quality.

The chemicals H_3PO_4, P_2O_5, PCl_3, and $POCl_3$ are all similar in that a gaseous intermediate or product is encountered somewhere in the reaction sequence. The synthesis of P_2S_5 resembles the above in that water and air must be completely absent in the whole or parts of the reaction sequence.

Sodium tripolyphosphate and the calcium phosphates are produced by the neutralization of phosphoric acid by alkaline slurries.

RAW MATERIALS

The following raw materials are used for each process:

Chemical	Raw Materials	
P_4 & Fe_2P	Phosphate Ore	Coke(C) SiO_2
H_3PO_4	P_4	O_2
P_2O_5	P_4	O_2
P_2S_5	P_4	S
PCl_3	P_4	Cl_2
$POCl_3$	PCl_3	Cl_2 (P_2O_5)
$Na_5P_3O_{10}$	H_3PO_4	Na_2CO_3 (NaOH)
Calcium Phosphates	H_3PO_4	$Ca(OH)_2$

When the nonphosphorus compounds are excluded, four subcategories become evident on the basis of raw material. The $POCl_3$ process is so like the PCl_3 process, however, that it is included in the latter subcategory.

PLANT SIZE AND AGE

Plant size will not affect the quantities of wastes produced (kg per kkg of product) to such a degree that subcategorization would be warranted. The same basic production processes for each chemical are used throughout the phosphate industry. Plant age will not affect the quantities of wastes produced to the degree where subcategorization is warranted. Another point is that there are no really new plants, and consequently the situation does not exist where new technologies make older technologies obsolete. With respect to economics it is particularly difficult to assess the effects of waste water treatment. The chemicals covered by this report serve as raw materials or intermediates for other products produced by the same company. The theoretical profitability of a single plant may well not decide if operations are to continue at that site. With this in mind it would be difficult if not impossible to establish criteria based on the economics of plant size or age for the purpose of subcategorization.

PRODUCT

The product does have some bearing on the waste water quality when the product or vapors from the product or intermediate come into contact with water. This topic has already been indirectly discussed under wastes generated. In summary, phosphorus production is associated with elemental phosphorus, phosphates, fluoride, suspended and dissolved solids. The production of H_3PO_4, P_2O_5, P_2S_5, PCl_3 and $POCl_3$ result in phosphates, dissolved solids, and acids in the waste waters. The production of $Na_2P_3O_{10}$ and the calcium phosphates result in phosphates, suspended and dissolved solids in the effluent.

LAND AVAILABILITY

Removal of suspended solids from raw waste waters is most easily accomplished by use of large settling ponds. This will be the principle concern for land availability. The plants in this category are located, however, in rural sites where the problem of land availability is minimized.

AIR POLLUTION CONTROL EQUIPMENT

All of the chemicals covered in this study use wet scrubbers or water systems in the process itself which amount to scrubbers. Therefore this is not a topic for subcategorization. Furthermore, it is recommended that dry air pollution control equipment either precede or replace wet scrubbers in order to reduce scrubber water contamination. Volatilization of hazardous substances such as fluorine from neutralization and settling ponds is insignificant.

SUBCATEGORIES

The factors that entered into the selection of subcategories are: wastes generated, treatability of waste waters, product, and particularly raw material and manufacturing process. Three subcategories were considered necessary for purposes of establishing effluent limitations guidelines:

a. Phosphorus Production
  1. phosphorus
  2. ferrophosphorus

b. Phosphorus Consuming
  1. phosphoric acid (dry process)
  2. phosphorus pentoxide
  3. phosphorus pentasulfide
  4. phosphorus trichloride
  5. phosphorus oxychloride

c. Phosphate
  1. sodium tripolyphosphate
  2. Calcium phosphates
    i. animal feed grade
    ii. food grade

SECTION V

WATER USE AND WASTE CHARACTERIZATION

INTRODUCTION

With the background of manufacturing technology discussed in Section III, this section discusses the specific water uses in the phosphate manufacturing industry and the raw wastes from this industry before control and/or treatment of these wastes. Both Section III and Section V are intended to be generally descriptive of the industry; i.e., they outline the standard manufacturing processes and the standard raw waste loads that are common to the great bulk of plants in the industry. It is not until Section VII, Control and Treatment Technology, and Section IX, Best Practicable Control Technology Currently Available, that distinctions are made (and quantitatively supported by independently verified sampling data of plant effluents) within the industry, pointing out those notable plants which have already achieved significant reduction or total elimination of polluting discharges.

The following discussion therefore, should not be taken as implying that the raw waste loads quoted are always actual plant discharges. Rather, they are intended to describe the total waste management problem originally faced by any plant in the industry. In actuality, significant abatement steps have been taken by some plants within the industry. By fully explaining the total waste management problem (in terms of raw waste loads), the control and treatment steps can be later explained and evaluated.

SPECIFIC WATER USES

Water is primarily used in the phosphate manufacturing industry for eight principal purposes:

Non-contact Cooling Water
Process and Product Water
Transport Water
Contact Cooling or Heating Water
Atmospheric Seal Water
Scrubber Water
Auxiliary Process Water
Miscellaneous Uses

Non-Contact Cooling Water

This type of water is used without contacting the reactants, such as in a tube-in-shell heat exchanger. If, however, the water contacts the reactants, then contamination of the water results and the waste load increases. Probably the single most important process waste control technique, particularly for subsequent treatment feasibility and economics, is segregation of non-contact cooling water from process water.

Non-contact cooling water is generally of two types in the industry. The first type is recycled cooling water which is cooled by cooling towers or spray ponds. The second type is once-through cooling water whose source is generally a river, lake, or tidal estuary, and the water is returned to the same source from which it was taken.

The only waste effluent from the recycled water would be water treatment chemicals and the cooling tower blowdown which generally is discharged with the cooling water. The only waste effluent from the once-through cooling water would be water treatment chemicals which are generally discharged with the cooling water. The cooling tower blowdown may contain phosphates, nitrates, nitrites, sulfates and chromates. The water treatment chemicals may consist of alum, hydrated lime, and alkali metals such as sodium and potassium produced by ion exchange units. Regeneration of the ion exchange units is generally accomplished with sodium chloride or sulfuric acid, depending on the type of unit employed in the plant.

Process and Product Water

The process or product water generally is that which comes in contact with the product and stays with the product as an integral part, such as the quenching, hydrolysis and dilution water used in phosphoric acid manufacture, or the water used as a reaction medium in food grade dicalcium phosphate manufacture.

Transport Water

Water may be used for transporting reactants or products between unit operations. An example is the use of water for transferring (by displacement) liquid phosphorus. Another example is the transfer of electrostatic precipitator dust in phosphorus manufacture as a slurry in water.

Since intimate contact between the process materials and transport water occurs, this water may generally contain dissolved or suspended materials and so is classified as process water.

Contact Cooling or Heating Water

This water comes under the general heading of process water because it comes in direct contact with process waters. A prime example is the large quantity of water used to quench the slag from phosphorus furnaces; another is the water used to condense the gaseous phosphorus after it is produced in the furnaces.

Other direct contact cooling or heating water use such as that for contact steam heating and/or drying, steam distillation, pump and furnace seals, etc., is generally of much lower volume than the barometric condenser water and is easier to treat for waste effluents.

Atmospheric Seal Water

Because some of the materials in this industry spontaneously ignite on contact with the oxygen in air, the air is kept out of reaction vessels with a water seal. Liquid phosphorus is universally protected by storing under a water blanket. These seal waters are considered as process waters.

Scrubber Water

Throughout this industry, water scrubbers are used to remove process vapors and/or dusts from tail gases and from gaseous process streams. The used scrubber water is regarded as process water since direct and intimate contact has occurred. The resultant solution or suspension may contain impurities or may be too dilute a solution to reuse or recover and thus is discharged.

Auxiliary Process Water

This water is used in medium quantities by the typical plant for auxiliary operations such as ion exchange regeneration, make-up water to boilers with a resultant boiler blowdown, equipment washing, storage and shipping tank washing, and spill and leak washdown. The volume of waste water from these operations is generally low in quantity but highly concentrated.

Miscellaneous Water Sources

These water sources vary widely among the plants originating from floor washing and cleanup, safety showers, eye wash stations, sanitary uses and storm run-off. The resultant streams are either non-contaminated or slightly contaminated with wastes. The general practice is to discharge such streams without treatment except for sanitary waste.

PROCESS WASTE CHARACTERIZATION

The descriptions of the manufacturing processes in Section III, and the flow diagrams included in that Section, qualitatively discussed the sources of wastes. The following discussion is intended to describe these waste streams both in quantity and in composition. These waste streams are the "raw" wastes before control or treatment (which is separately discussed in Section VII).

Aqueous wastes emanating from air pollution abatement equipment are considered as process wastes in this study.

The following sections quantify the raw process wastes in each segment of the industry. A discussion of the source, nature, and amount of these wastes for each segment is followed by a table summarizing the standard raw waste load.

Various plants in the industry differ significantly in the degree of process and cooling water recirculation. Hence, the waste water quantities and constituent concentrations quoted may be grossly different from plant-to-plant. However, the raw loads in kg per kkg of product (lb/ton) are dependent primarily on the manufacturing processes and are therefore much more representative of the entire industry.

The Phosphorus Production Subcategory

The discussion of phosphorus manufacturing technology in Section III and the flow diagram of Figure 2 qualitatively pointed out the following streams emanating from the process (in addition, of course, to the phosphorus product stream):

By-products: Slag, Ferrophosphorus, and Carbon Monoxide
Non-contact Cooling Water
Electrostatic Precipitator Dust
Calciner Precipitator Dust
Calciner and Furnace Fume Scrubber Liquor
Phosphorus Condenser Liquor (Aqueous phase)
Phosphorus Sludge (or mud)
Slag Quench Liquor

The following sections discuss each of the above in quantitative detail, and identify which are typically returned to the process and which are classified as raw waste streams from the manufacturing operation.

By-product Streams

The by-products of the phosphorus manufacturing operation are:

	kg/kkg	lb/ton
Ferrophosphorus	300	600
Slag ($CaSiO_3$)	8,900	17,800
CO gas	2,800	5,600

Both ferrophosphorus and slag are sold, and the carbon monoxide is either used to generate heat in the process or is otherwise burned on site. Hence, none of the above three materials is considered a waste.

The quench water used for the by-product slag is separately discussed as a waste stream.

The by-product ferrophosphorus is cast as it is tapped from the furnace and air-cooled. The solids are then broken up and shipped. No water is used specifically for ferrophosphorus, and there are no wastes accountable for ferrophosphorus manufacture.

Non-Contact Cooling Water

Phosphorus production facilities generate huge quantities of heat. The electrical power consumption is approximately 15,500 kwh/kkg (48 million Btu/ton). An additional 8,100 kwh/kkg (25 million Btu/ton) are generated by combustion of the by-product carbon monoxide. Some of this energy, 6,100 kwh/kkg (19 million Btu/ton), is absorbed in the endothermic furnace reaction, and some is absorbed by the endothermic calcining operation. Other portions of this energy are released to the atmosphere by burning of waste carbon monoxide (that not used for calcining) and by convection, radiation and evaporative losses from the equipment and process materials. Still other portions are absorbed by contact waters in the calcining process and furnace from scrubbers, in the phosphorus condenser, and in the slag quenching operation.

After accounting for the above energy demands, a significant quantity of heat is absorbed by non-contact cooling water for the furnace shell, the crucible bottom, the fume hood, the tap holes, the electrode fixtures, the electrical transformer, and for any indirect phosphorus condensation. The quantity of this water is highly variable from plant to plant, and depends on the furnace design, the furnace size, and the degree of recirculation (through heat exchangers with other water streams or through cooling towers), whether or not cooling water is used in series for different requirements, the inlet temperature of the available cooling water, and the ambient air temperature. Plant 181 uses 325,000 l/kkg of product (78,000 gal/ton); Plant 159 uses 38,000 l/kkg (9,000 gal/ton); and TVA at Muscle Shoals, Alabama,(5) uses 130,000 l/kkg (31,000 gal/ton).

Electrostatic Precipitator Dust

The high-temperature electrostatic precipitator removes dusts from the furnace gases before these gases are condensed for recovery of phosphorus. These dusts may contain up to 50 percent P_2O_5, and therefore find value either as a fertilizer for sale or for return to the process. In the latter case, they are transported to the ore blending head end of the plant. One TVA scheme slurries the dust for transport; the slurry is pumped to a settling pond, the settled solids are fed to the ore - blending unit, and the pond overflow is reused in the slurrying operation.

The quantity of precipitator dust is approximately 125 kg/kkg of product (250 lb/ton). Regardless of the method of sale or reuse, the precipitator dust is not a waste material to be disposed of from the plant.

Calciner Precipitator Dust

Dry dust collectors are used in the calcining operation, upstream of wet scrubbing systems. The dry fine dusts collected are recycled directly to the sizing and calcining operations. The collected and recycled fines may amount to as much as 30 percent of the net production from the nodulizing process.

There is no plant discharge of dry calciner precipitator dusts; therefore this is not a component of the plant's raw waste load.

Calciner and Furnace Fume Scrubber Liquor

Water scrubbers are used for air pollution abatement for the calciner exhaust stream (downstream of dry dust collection), for furnace fumes, for ore sizing dusts, for coke handling dusts, for raw material feeding operation dusts, and for furnace taphole (slag and ferrophosphorus) fumes. The scrubber liquor contains suspended solids (which are mainly SiO_2 and Fe_2O_3), some phosphates and sulfates as dissolved solids, and a large quantity of fluorides. To explain the presence of these fluorides in the scrubber liquor, Table 6 lists the quantities of materials in commercial phosphate rock presented as pounds per ton of phosphorus ultimately produced after normalizing of 26 percent P_2O_5 content. From Table 6, the average quantity of F in ore is 275 kg/kkg of P_4 (550 lb/ton). Approximately 8 percent of this quantity of F, or 22 kg/kkg (44 lb/ton), is volatilized in the ore calcining operation, and is subsequently a constituent of the scrubber liquor.

This scrubber liquor is highly acidic for three reasons: the sulfur (as SO_3) forms sulfuric acid; the P_2O_5 forms phosphoric acid; and the fluorine, which is released in the form of silicon tetrafluoride, forms fluosilicic acid and silicic acid on hydrolysis.

The quantity of scrubber liquor wasted depends on the degree of recirculation of this liquor from a sump back to the scrubbers. TVA at Muscle Shoals circulates approximately 21,000 l/kkg of

TABLE 6

Composition of Commercial Phosphate Rocks (12)

Expressed as kg per kkg (lb/ton) of Phosphorus Produced

Constituent	Florida Land Pebble Furnace Grade		Tennessee Brown Rock Furnace Grade		Western Phosphoric Acid Low Grade	
	kg/kkg	lb/ton	kg/kkg	lb/ton	kg/kkg	lb/ton
P_2O_5	2,600	5,200	2,600	5,200	2,600	5,200
CaO	3,800	7,600	3,550	7,100	3,150	6,300
MgO	35	70	75	150	190	380
Al_2O_3	125	250	1,230	2,460	810	1,620
Fe_2O_3	155	310	760	1,520	550	1,100
SiO_2	725	1,450	3,150	6,300	3,750	7,500
SO_3	215	430	50	100	260	520
F	305	610	270	540	245	490
CO_2	330	660	150	300	550	1,100
Organic Carbon	40	80	35	70	685	1,370
Na_2O	10	20	35	70	205	410
K_2O	10	20	50	100	135	270

product (5,000 lb/ton) with a portion bled off to control the composition. This scrubber liquor is of the following composition:

Constituent	Concentration, %
F	3.1
SiO_2	1.1
P_2O_5	0.2
Fe_2O_3	0.1
S	1.7

If the fluoride concentration of 3.1 percent is equated to a standard raw waste load (as previously discussed) of 22 kg/kkg (44 lb/ton), the quantities of other scrubber liquor components may be calculated:

Constituent	Raw Waste Load	
	kg/kkg	lb/ton
F	22	44
SiO_2	8	16
P_2O_5	1.5	3
Fe_2O_3	0.5	1
S	12	24

The total $CaCO_3$ acidity of the scrubber liquor, calculated from the above constituent quantities, is 60 kg/kkg (120 lb/ton).

Other plants do not recirculate scrubber liquor; the volume wasted is much greater and the constituent concentrations are much smaller, but the raw waste loads (in kg/kkg of product) should be comparable. Plant 181 does not directly recirculate the liquor, and uses 300,000 l/kkg (71,000 gal/ton) for scrubbing.

Phosphorus Condenser Liquor

The furnace gases pass from the electrostatic dust precipitator to the phosphorus condenser, where a recirculating water spray condenses the product. The condenser liquor is maintained at approximately 60°C (140°F), high enough to prevent solidification of the phosphorus (freezing point 44°C (112°F)). This condenser liquor is "phossy water", essentially a colloidal dispersion of phosphorus in water, since the solubility at 20°C (68°F) is only 3.0 mg/l. Depending on how intimate the water/phosphorus contact was, the phosphorus content of phossy water may be as high as several weight percent.

The condenser liquor also contains constituents other than elemental phosphorus: fluoride, phosphate, and silica. Using the average F content of ore (from Table 6) of 275 kg/kkg, plus the estimate that 12 percent of the F in the ore volatilizes in the furnace and is therefore equivalent to 33 kg/kkg (66 lb/ton), and by accounting for 6 kg of F per kkg (12 lb/ton/ ton) which is collected in the precipitator dust and in the phosphorus sludge ash, a raw waste load of F is derived of 27 kg/kkg (54 lb/ton) in the condenser liquor. This condenser liquor is not acidic despite the hydrolysis of P_2O_5 and SiF_4 to H_3PO_4, H_2SiF_6, and H_2SiO_3 because aqueous ammonia or caustic is added to prevent undue corrosion in the condenser.

There are other sources of phossy water within the plant. Storage tanks for phosphorus have a water blanket, which is discharged on phosphorus transfer. Railroad cars are cleaned by washing with water. Phosphorus may be purified by washing with water. Together, all sources of phossy water wastes amount to about 5,400 l/kkg (1,300 gal/ton), and at a concentration of 1,700 mg/l, the quantity of phosphorus wastes amounts to about 9 kg/kkg produced (18 lb/ton), as reported by TVA.

At TVA, the condenser liquor is recirculated at the rate of 33,000 l/kkg (8,000 gal/ton). Other plants may differ significantly in the quantity of phossy water circulated, but the raw wastes (in kg/kkg of product) should be fairly uniform. For example, Plant 181, which does not directly recirculate its condenser water, uses 84,000 l/kkg (20,000 gal/ton), with an additional 17,000 l/kkg (4,000 gal/ton) for phosphorus handling and storage.

To calculate the raw waste loads of phosphate and silica in the condenser liquor, the following TVA recirculated-liquor composition was used:

Constituent	Concentration, %
F	8.3
P_2O_5	5.0
SiO_2	4.2

Equating 8.3 percent F with the previously-derived 27 kg/kkg of F, the raw waste loads of P_2O_5 and SiO_2 become respectively 16.5 kg/kkg (33 lb/ton) and 13.5 kg/kkg (27 lb/ton).

Phosphorus Sludge

In addition to phossy water, the phosphorus condenser sump also collects phosphorus sludge, which is a colloidal suspension typically 10 percent dust, 30 percent water and 60 percent phosphorus. The quantity of sludge formed is directly dependent on the quantity of dust that escapes electrostatic precipitation, hence the very large investment made for highly efficient precipitators.

Using 125 kg of dust (per kkg of product) collected by the electrostatic precipitator, and assuming a 98 percent collection efficiency, the dust reaching the condenser amounts to 2.5 kg/kkg

(5 lb/ton). If all of this dust became part of the sludge, the sludge quantity would be 25 kg/kkg (50 lb/ton) of product, and it would contain 15 kg/kkg (30 lb/ton) of elemental phosphorus.

This sludge is then universally processed for recovery of phosphorus, typically by centrifugation. A 96 percent recovery has been reported, with the product (subsequently returned to the process) averaging 92 to 96 percent phosphorus. The remaining 4 percent of the phosphorus in the sludge is burned in a phosphoric acid unit, so that no wastes emanate from the plant.

Other methods for processing the sludge which also result in no plant effluent include heating in a slowly rotating drum in an inert atmosphere to drive off phosphorus vapor, which is then condensed with a water spray into a sump. The solid residue obtained is completely free of elemental phosphorus and can be safely landfilled or recycled to the feed preparation section of the plant.

Slag Quenching Liquor

Slags from phosphorus furnaces are mainly SiO_2 and CaO, and would also contain Al_2O_3, K_2O, Na_2O, and MgO in amounts consistent with the initial ore composition. In addition to these oxides, phosphate rock may contain 0.1-0.2 kg/kkg (0.2-0.4 lb/ton) of uranium in the ore, and the radiation levels of both the slag and the quench waters must be appropriately noted. Other constituents of the slag presenting problems for quench water pollution control are fluoride and phosphate. Approximately 80 percent of the original F in the phosphate rock, 220 kg/kkg of P_4 (440 lb/ton), referring to Table 6, winds up in the slag. About 2.7 percent of the original P_2O_5 in the phosphate rock, 70 kg/kkg (140 lbs/ ton), winds up in the slag.

At Plant 181, approximately 24,600 l/kkg (5,900 gal/ton) may be used for quenching the slag, with the slag quench liquor having the following composition and raw waste loads:

Constituent	Concentration, mg/l	Raw Waste Load	
		kg/kkg P_4	lb/ton P_4
Total Suspended Solids	800	20	40
Total Dissolved Solids	1,700	42	85
Phosphates (as P)	12	0.3	0.6
Sulfate (as S)	1,000	25	50
Fe	14	0.35	0.7
F	170	4.5	9
Total Alkalinity	230	5.5	11

TABLE 7

Summary of Raw Wastes from Phosphorus Manufacture

Note: Waste water quantities and constituent concentrations are highly variable, depending on degree of recirculation, but the raw waste loads should be representative.

	Calciner Scrubber Liquor	Phosphorus Condenser Plus Other Phossy Water	Slag Quenching Water	Composite Waste
Waste Water Quantity,				
l/kkg	300,000	100,000	25,000	425,000
gal/ton	72,000	24,000	6,000	102,000
Raw Waste Load, kg/kkg				
TSS	8.5	13.5	20.5	42.5
P_4	-	9	-	9
PO_4	2	22	1	25
SO_4	36	-	75	111
F	22	27	4.5	53.5
Total Acidity	60	-	-	54.5
Total Alkalinity	-	-	5.5	-
Raw Waste Load, lb/ton				
TSS	17	27	41	85
P_4	-	18	-	18
PO_4	4	44	2	50
SO_4	72	-	150	222
F	44	54	9	107
Total Acidity	120	-	-	109
Total Alkalinity	-	-	11	-
Concentrations, mg/l				
TSS	28	135	820	100
P_4	-	90	-	21
PO_4	7	220	40	59
SO_4	120	-	3,000	260
F	73	270	180	126
Total Acidity	200	-	-	128
Total Alkalinity	-	-	220	-

The Phosphorus Consuming Subcategory

No direct process aqueous wastes are generated in this segment of the industry. The raw wastes arise from phosphorus storage and transfer, from wet scrubbing of tail gases, from vessel cleaning, and from leaks and spills.

Phossy Water Wastes

Because phosphorus is transported and stored under a water blanket, phossy water is a raw waste material at phosphorus using plants as well as at phosphorus producing plants. The standard procedure when liquid phosphorus is transferred from a rail car to the using plant's storage tank is to pump the displaced phossy water from the storage tank back into the emptying rail car as practiced at Plants 037 and 192. Instead of being wasted at the phosphorus-using plant, the phossy water is shipped back to the phosphorus-producing facility for treatment and/or re-use. Therefore, standard raw phossy water wastes at the phosphorus using plants are due to surges or to anomalies in the storage tank water level control system rather than to the direct wasting of all displaced water.

A more insidious source of phossy water may arise at phosphorus consuming plants. Should reactor contents containing phosphorus ever be dumped into a sewer as a result of operator error, emergency conditions, or inadvertent leaks or spills, the phosphorus would remain at the low points in the sewer line generally as a solid (melting point 44°C (111°F)) and would contact all water flowing in that sewer from that time on. Since phosphorus burns when exposed to air (autoignition temperature 93°C), there is general reluctance to clean it out. The common practice is to ensure a continuous water flow to prevent fire.

The typical phosphorus loss for phosphorus consuming plants is 1 kg lost to phossy water per kkg consumed (2 lb/ton). Whenever phosphorus is tranferred by displacement, 580 liters of water are displaced per kkg of phosphorus (140 gal/ton). These values are equivalent to a phosphorus concentration of 1700 mg/l. For comparison, a typical phosphorus content in phossy water at a phosphorus producing plant has also been reported at 1700 mg/l.

Phosphoric Acid Manufacture

The production of phosphoric acid by the "dry" process from elemental phosphorus consumes a total of about 380 liters of water per kkg of product (92 gal/ton) for both the hydration and the acid dilution steps. The cooling water requirements are typically 92,000 liters per kkg of product (22,000 gal/ton); but with recycle of cooling water, the make-up cooling water requirement is approximately 4,600 liters per kkg of product (1,100 gal/ton). There is no aqueous process waste from notable phosphoric acid Plants 003, 006, 042, and 075. Despite good housekeeping at a notable plant, however, leaks or spills of phosphoric acid may amount to an average of 1 kg/kkg (2 lb/ton), with a range of 0 to 2.5 kg/kkg (0 to 5 lb/ton).

Where food grade phosphoric acid is produced, a standard raw waste of 0.1 kg/kkg (0.2 lb/ton) of arsenic sulfide is precipitated by addition of a soluble sulfide (H_2S, Na_2S, NaHS) and filtered out of the acid. An additional 0.75 kg/kkg (1.5 lb/ton) of filter-aid material may accompany the sulfide as a solid waste.

Phosphorus Pentoxide Manufacture

The waste water from the tail seals on the condensing towers typically contains 0.25 kg/kkg (0.5 lb/ton) of H_3PO_4 (100 percent basis). Approximately 500 l/kkg (120 gal/ton) of water may be used, resulting in a concentration of 470 mg/l for the effluent bleed.

The inlet air dryer silica gel is regenerated often, but is renewed very infrequently (perhaps every ten years). The wasted material is typically landfilled.

Approximately 29,000 l/kkg (7,000 gal/ton) of non-contact cooling water are used.

Phosphorus Pentasulfide Manufacture

The water seals on the batch reactor vent lines accumulate a mixture of phosphorus mud and lower phosphorus sulfides. These seals are cleaned once a week, and the residue amounts to 0.15 kg/kkg (0.3 lb/ton). This residue is hazardous and flammable and is typically buried.

Should any batch be aborted (a rare occurrence) because of agitator failure, cast iron pot failure, or other reason, the material is disposed of by incineration.

The dust collected by a cyclone from the P_2S_5 crushing operation amounts to 1 kg/kkg (2 lb/ton).

The still pot for the vacuum distillation step accumulates impurities, which include carbon and iron sulfur compounds and glassy phosphates. Most important, the residues contain arsenic pentasulfide, which is higher-boiling than the corresponding phosphorus pentasulfide. Arsenic occurs naturally with phosphorus (they are both Group V-A elements) at a level of about 0.075 kg/kkg (0.15 lb/ton) of arsenic which is equivalent to 0.05 kg of As_2S_5 per kkg of product P_2S_5 (0.1 lb/ton). The entire still pot residue is about 0.5 kg/kkg (1 lb/ton). Periodically, these residues are removed and the solids are broken up and buried. Approximately 17,000 l/kkg (4,000 gal/ton) of non-contact cooling water is used.

In the casting of liquid P_2S_5, the fumes from burning liquid (molten P_2S_5 auto-ignited) are scrubbed. Typically, the scrubber water contains 1.25 kg of combined P_2O_5 and SO_2 per kkg of product P_2S_5 (2.5 lb/ton). Because both P_2O_5 and SO_2 are absorbed by a water scrubber only with difficulty, the water flow rate is high, 30,000 l/kkg (7,200 gal/ton). These values reduce the concentrations of PO_2^{-3} and SO_3^{-2} in the scrubber effluent of 17 and 34 mg/l, respectively. Much lower scrubber flow rates could be used should weak caustic or lime be used instead of water.

Phosphorus Trichloride Manufacture

The batch or semicontinuous reactor/stills accumulate residues which are periodically but infrequently removed. These residues contain arsenic trichloride, which is higher-boiling than the corresponding phosphorus trichloride. Arsenic occurs naturally with phosphorus (they are both Group V-A elements) at a level of about 0.075 kg/kkg (0.15 lb/ton) of arsenic, which is equivalent to 0.05 kg of $AsCl_3$ per kkg of product PCl_3 (0.1 lb/ton). This is about half the quantity of total residue in the stills (exclusive of residual PCl_3 from the last batch or run before shutdown).

The average non-contact cooling water requirement is 54,000 l/kkg (13,000 gal/ton).

Water scrubbers collect PCl_3 vapors from the reaction, the product distillation, the product storage, and the product transfer operations and hydrolyze these vapors to HCl and to H_3PO_3 (which may subsequently be oxidized to H_3PO_4). The quantity of PCl_3 collected is highly dependent on the efficiency of the upstream condensers, since PCl_3 is highly volatile:

Temp, °C	Temp, °F	PCl3 Vapor Pressure, mm Hg(27)
20	68	99
40	104	235
60	140	690
76	169	760

At Plant 037, sufficient heat transfer area was provided in the condensers to limit the raw waste load to 3 kg of HCl plus 2.5 kg of H_3PO_3 per kkg of product PCl_3 (6 lb/ton and 5 lb/ton). Approximately 5,000 l/kkg (1,200 gal/ton) of scrubber water were used to collect these wastes. Other smaller waste quantities of HCl and H_3PO_3 generated from tank car and returnable container cleaning operations have been included in these quantities.

These quantities are based on the most reliable data available at Plant 037, overall material balances of product PCl_3 shipped vs. elemental phosphorus received. These data, validated over long periods of time for profitability purposes, show a total loss of phosphorus trichloride of 5 kg/kkg (10 lb/ton). An estimated breakdown of this loss is:

Transfer and Storage of Phosphorus,	1.0 kg/kkg (2 lb/ton)
Reactor/Still Residues,	0.1 kg/kkg (0.2 lb/ton)
Scrubber for Distillation Tail Gases,	2.5 kg/kkg (5 lb/ton)
Transfer of PCl_3,	1.0 kg/kkg (2 lb/ton)

Other than the estimated loss of elemental phosphorus and the reactor/still residues, the losses which become water-borne raw wastes amount to 3.5 kg/kkg (7 lb/ton). Upon hydrolysis, this stoichiometrically becomes 3 kg/kkg (6 lb/ton) of HCl plus 2.5 kg/kkg (5 lb/ton) of H_3PO_3. These material-balance data have been used because of their long-term confirmation. Direct measurements of waste water flow rates and of waste water constituent analysis were not relied on in this case since accurate flow rate measurements were not possible in the existing plant configuration and since no statistically meaningful analytical data had been collected. The acid wastes from washing tank cars and tank trucks and from washing used $POCl_3$ filter elements are very small at present. Water use data taken from Plant 037, supplemented by an independent analysis of the waste water, yielded the results in Table 8. Total raw waste generated in truck-loading, in tank-car cleaning, and in filter-element washing is 0.014 kg/kkg (0.028 lb/ton) of HCl plus 0.003 kg/kkg (0.007 lb/ton) of total phosphates.

Phosphorus Oxychloride Manufacture

The water scrubber for the distillation operation in the standard process (using P_2O_5 and Cl_2) typically collects 1.5 kg of HCl (anhydrous basis) and 0.25 kg of H_3PO_4 (100 percent basis) per kkg of product $POCl_3$ (3 lb/ton and 0.5 lb/ton), and the scrubber for $POCl_3$ transferring collects about 0.2 kg of HCl and 0.15 kg of H_3PO_4 per kkg of product (0.4 lb/ton and 0.3 lb/ton). Allowing for small wastes from returnable container cleaning operations, the standard raw waste load is 2 kg of HCl and 0.5 kg of H_3PO_4 per kkg of product (4 lb/ton and 1 lb/ton). Approximately 2,500 l/kkg (600 gal/ton) of water are used, so that the raw waste concentrations are 800 mg/l HCl and 200 mg/l H_3PO_4.

The source of the above data on raw waste loads was Plant 147 records and plant personnel analysis of these records. An independent verification of these results was not judged valid since at this plant neither an accurate determination of waste water flow rate nor the collection of a distinct waste water sample from each unit operation contributing to the waste load was practical, and since statistically valid background data were not at hand.

These waste quantities for $POCl_3$ manufacture are somewhat smaller than for PCl_3 manufacture since $POCl_3$ is less volatile (boiling point 107°C). In the batch process, the refluxing liquid is all PCl_3 at the start, but becomes increasingly richer in $POCl_3$.

TABLE 8

Minor Wastes from Plant 037 (PCl3 and POCl3)

		Truck-Loading Vent Scrubber	Tank Car Cleanout Water	Filter Element Washout Drum
Water Use:	l/kkg	8.8	10.5	0.46
	gal/ton	2.1	2.5	0.11
Constituent Analysis, mg/l:				
	Chloride	340	715	6,480
	Total PO_4	260	26	590
	Total Acidity	660	-	18,200
Raw Waste Load, kg/kkg:				
	Chloride	0.0030	0.0075	0.0030
	Total PO_4	0.0023	0.0003	0.0003
	Total Acidity	0.0058	--	0.0083
Raw Waste Load, lb/ton:				
	Chloride	0.006	0.015	0.006
	Total PO_4	0.005	0.001	0.001
	Total Acidity	0.012	--	0.017

The air-oxidation process presents a much more difficult task for the reflux condenser, since the vapors are highly diluted with non-condensibles. With the use of refrigerated condensers, however, the measured raw waste load is no different for this process. At Plant 037, data collected over three months from the reactor/still scrubber for $POCl_3$ manufacture, which had an estimated flow rate of 1,800 l/kkg (430 gal/ ton), had average net values of:

Chloride	669 mg/l
$CaCO_3$ acidity	1,213 mg/l

These data reduce to a raw waste of 1.2 kg/kkg (2.4 lb/ton) of HCl plus 0.35 kg/kkg (0.7 lb/ton) of H_3PO_4, which are extremely close to the corresponding values for Plant 147.

Where product $POCl_3$ is filtered, the used filter elements are first washed to hydrolyze the residual $POCl_3$. Disposable elements are then landfilled. The quantity of filtered solids retained on the elements is only a very small fraction of the weight of the used element. The elements are washed in a 55-gallon drum, so that a very small quantity of waste water (and of acid wastes) is involved compared to the scrubber waste load. Although there is no continuous withdrawal of residues from $POCl_3$ distillations, very little residue accumulates. Twice a year this residue (mostly glassy phosphates) is washed out with hot water.

The non-contact cooling water requirement for $POCl_3$ manufacture by either the standard or the alternate method is approximately 50,000 l/kkg (12,000 gal/ton).

Variability of Raw Wastes from the Production of Phosphorus Trioxide and Phosphorus Oxychloride

The data below indicate the variability of concentrations in the raw waste load at Plant 037.

Date (1973)	$CaCO_3$ Acidity, mg/l	Chloride, mg/l
2/27	1170	560
2/28	1220	603
3/1	1720	822
4/19	850	447
4/23	480	305
4/24	950	532
4/25	1430	851
4/26	1250	589
4/27	1300	1035
4/30	1120	518
5/1	1470	1040
5/2	1690	716
5/3	280	773
5/4	1340	603
5/7	1810	1000
5/8	1220	574
5/9	1290	716
Mean	1217	687
Std. Deviation	384	208
Std. Deviation	384	208
95% Conf. Int. (Single Day)	+_814	+_441

In this case, there was no damping capacity; the acidity and chloride concentrations were closely coupled to the manufacturing process. The comparison of the 95% confidence intervals with the daily data show only one point of 17 (for acidity) and no points outside (for chloride).

Based on these very limited samples of data, it appears that the classical statistics may be applied, but with extreme caution.

For the above sets of data from Plant 037, a value of $(X + 3\sigma) / X$ might represent a maximum allowable daily reading as a multiple of the mean:

Parameter	$(X + 3\sigma) / X$
Acidity Concentration	1.95
Chloride Concentration	1.91

This maximum allowable value would be extremely liberal, since a Students "t" value of 3 is equivalent to less than one reading in 100 being unduly rejected. To be even more liberal (since the data base for this analysis is extremely skimpy), the maximum value from the above table will be assumed, so that the effluent limitation guideline for the manufacture of PCl_3 and $POCl_3$ should be a maximum daily value no greater than twice the mean (as represented by consecutive 30-day averages).

pH can be controlled much more closely than other parameters. Hence, it is recommended that the pH limitation be met at all times.

TABLE 9

Summary of Raw Waste from Phosphorus-Concuming Plants

	H_3PO_4 (75%)	P_2O_5	P_2S_5	PCl_3	$POCl_3$
Phossy Water: P_4 conc, ppm	1,700	1,700	1,700	1,700	--
l/kkg P_4 consumed	580	580	580	580	--
kgP_4/kkg P_4 consumed	1	1	1	1	--
gal/ton P_4 consumed	140	140	140	140	--
lb /ton P_4 consumed	2	2	2	2	--
Process Water Wasted: l/kkg Pdt	--	500	30,000	5,000	2,500
gal/ton Pdt	--	120	7,200	1,200	600
Raw Waste Load, kg/kkg Pdt:					
HCl	--	--	--	3	2
H_2SO_3	--	--	1	--	--
$H_3PO_3 + H_3PO_4$	1	0.25	0.5	2.5	0.5
Raw Waste Load, lb /ton Pdt:					
HCl	--	--	--	6	4
H_2SO_3	--	--	2	--	--
$H_3PO_3 + H_3PO_4$	2	0.5	1	5	1
Concentrations, **mg/l**: HCl	--	--	--	600	800
H_2SO_3	--	--	34	--	--
$H_3PO_3 + H_3PO_4$	High	470	17	500	200
Process Water Consumed·					
l/kkg Pdt.	380	--	--	--	--
gal/ton Pdt	92	--	--	--	--
Cooling Water Used: l/kkg Pdt	91,000	29,000	16,600	54,000	50,000
gal/ton Pdt	22,000	7,000	4,000	13,000	12,000
Solid Wastes, kg/kkg Pdt:					
As Compounds	0.1	--	0.05	0.05	--
Total Residues	--	--	0.7	0.05	<0.05
Solid Wastes, lb /ton Pdt:					
As Compounds	0.2	--	0.1	0.1	--
Total Residues	--	--	1.4	0.1	<0.1

The Phosphate Subcategory

The aqueous wastes from this segment of the industry arise from the use of wet dust scrubbing equipment for the finely divided solid products, and from processes which use excess process water which may become a waste stream.

Sodium Tripolyphosphate Manufacture

Exemplary Plants 006, 042, and 119 have no process wastes. The dust collected from the spray dryer gaseous effluent stream is added to the spray dryer solid product stream. The water used for subsequent scrubbing of this gas stream from the spray dryer is then recycled to the mix area and is used as process water in the neutralization step. The cooling air used for the product tempering is vented into the spray dryer vent line upstream of the scrubbing operation.

The neutralization step requires a total of 1,040 l/ kkg (250 gal/ton), of which 290 l/kkg (70 gal/ton) are recycled from the scrubber. Make-up water, 750 l/kkg (180 gal/ton), is added since water is evaporated in the product drying step. The make-up water is softened, and regeneration of the softener combined with boiler and cooling tower blowdowns amounts to 210 l/kkg (50 gal/ton), 70 percent of which is from water treatment regeneration and 30 percent from blowdowns. These blowdown wastes typically contain 1,500 mg/l of dissolved chlorides.

Calcium Phosphates

The raw aqueous wastes from the manufacture of food grade calcium phosphates are from two primary and approximately equal sources: the centrate of filtrate from dewatering of the dicalcium phosphate slurry and the effluent from wet scrubbers which collect airborne solids from product drying operations. Both of these sources contain suspended, finely-divided calcium phosphate solids. It is normal practice in an integrated plant to partially recycle the scrubber water and to partially use the DCP centrate or filtrate as make-up scrubber water, as at Plant 003. The total raw wastes from this system are typically 4,200 l/kkg (1,000 gal/ton) containing 100 kg/kkg (200 lb/ton) of solids (a concentration of 2.4 percent). An additional 30 kg/kkg (60 lb/ton) of dissolved solids (0.7 percent of this waste stream) originates from phosphoric acid mists in the scrubbers and from excess phosphoric acid in the reaction liquid.

For non-food grade dicalcium phosphate plants, the water scrubbers which collect airborne solids normally operate at partial recycle. Since there is no waste from a dewatering operation, and since dry dust collection typically precedes wet scrubbing, the raw wastes are considerably smaller than for the food grade operation. Dry dust collection is typical since only one or two products are made, so that the collected solids may be added directly to the product stream without extensive segregation.

Moreover, since purity requirements are considerably less severe, the product stream can tolerate such additions. With the above measures, the wet scrubber wastes are typically 420 l/kkg (100 gal/ton) containing 22.5 kg/kkg (45 lb/ton) of suspended solids (a concentration of 5 percent) plus 4 kg/kkg (8 lb/ton) of dissolved phosphates from acid mists (0.7 percent). At Plant 182, this bleed stream from the wet scrubber recirculation system is charged directly to the neutralization reactor; hence, this plant had no discharge. As an added feature, this notable plant used cooling water blowdown as make-up to the airborne-solids scrubbing system, thereby eliminating all aqueous discharges (except for the effluent from regeneration of the water softener).

For the non-food grade plants, however, acid defluorination is an additional source of raw wastes (unless already defluorinated acid is delivered to the plant). Wet-process phosphoric acid (54 percent P_2O_5) contains approximately 1 percent fluorine. Upon silica treatment, 13.5 kg per kkg of acid (27 lb/ton), or 10.5 kg of silicon tetrafluoride product dicalcium phosphate dihydrate (21 lb/ton), are liberated. When hydrolyzed in the acid scrubber, the raw waste contains 12 kg/kkg product (24 lb/ton) of combined fluosilicic acid (H_2SiF_6), hydrofluoric acid (HF) and silicic acid (H_2SiO_3). These raw wastes are contained in a scrubber water flow of 6,300 liters/ kkg (1,500 gal/ton), so that the combined concentration of fluosilicic acid, hydrofluoric acid and silicic acid is 1,900 mg/l. For any plant manufacturing calcium phosphates of any grade, non-contact cooling water is used in reactors and/or in dried product coolers.

Other possible sources of aqueous wastes are regeneration of water softeners and storm water runoff (all exterior surfaces of calcium phosphate plants become coated with fine lime and/or phosphate dusts).

In dry product plants, a significant housecleaning effort must be continually maintained. In non-food grade calcium phosphate plants, the dry product sweepings (from dust, spills, etc.) are added to the process stream. In food grade plants, however, the sweepings (consisting of lime, lime grit, and calcium phosphates) are wasted. Typically, this solid waste amounts to 10 kg/kkg (20 lb/ton).

TABLE 10

Summary of Raw Wastes from Phosphate Plants

	Sodium Tripoly-Phosphate	Food Grade Calcium Phosphates		Animal Feed Calcium Phosphates	
		Dewatering	Solids Scrubbing	Acid Defluorination	Solids Scrubbing
Process Water Wasted:					
l/kkg Pdt	0	2,100	2,100	6,300	420
gal/ton Pdt	0	500	500	1,500	100
Raw Waste Load, kg/kkg Pdt:					
TSS	-	50	50	-	22.5
Dissolved PO_4	-	15	15	-	4
HF, H_2SiF_6, H_2SiO_3	-	-	-	12	-
Raw Waste Load, lb/ton Pdt:					
TSS	-	100	100	-	45
Dissolved P_4	-	30	30	-	8
HF, H_2SiF_6, H_2SiO_3	-	-	-	24	-
Concentrations, mg/l:					
TSS	-	24,000	24,000	-	54,000
Dissolved PO_4	-	7,000	7,000	-	7,000
HF, H_2SiF_6, H_2SiO_3	-	-	-	1,900	-
TDS, mg/l	-	7,000	7,000	1,900	7,000
Solid Wastes:					
kg/kkg Pdt	0	10		-	-
lb/ton Pdt	0	20		-	-

SECTION VI

SELECTION OF POLLUTION PARAMETERS

INTRODUCTION

Section V of this report quantitatively discussed the raw wastes generated in the phosphate manufacturing industry. The following were identified as being constituents of the industry's process waste waters:

Suspended Solids
Phosphate and Elemental Phosphorus
Sulfates and Sulfites
Fluoride
Chloride
Dissolved Solids
pH, Acidity and Alkalinity
Temperature
Arsenic
Vanadium, Cadmium, and Radioactivity

The following discussion examines each of the above constituents and their impact on receiving waterways from a chemical a physical and a biological viewpoint. Additional constituents such as hexavalent chromium, iron, alkalinity, and hardness, which are of typical concern whenever blowdowns from cooling towers, boilers and water treatment facilities are involved, are noted here but are not discussed in detail in this study (which deals more specifically with the process wastes of the phosphate industry).

PROPERTIES OF THE POLLUTANTS AND POLLUTANT PARAMETERS

The following paragraphs describe the chemical, physical and biological properties of the pollutants and pollutant parameters that exist for this industry. The undesirable characteristics that these parameters exhibit or indicate are stated, giving reason to why they were selected.

TOTAL SUSPENDED SOLIDS

Suspended solids include both organic and inorganic materials. The inorganic components include sand, silt, and clay. The organic fraction includes such materials as grease, oil, tar, animal and vegetable fats, various fibers, sawdust, hair, and various materials from sewers. These solids may settle out rapidly and bottom deposits are often a mixture of both organic and inorganic solids. They adversely affect fisheries by covering the bottom of the stream or lake with a blanket of material that destroys the fish-food bottom fauna or the spawning ground of fish. Deposits containing organic materials may also deplete bottom oxygen supplies and produce hydrogen sulfide, carbon dioxide, methane, and other noxious gases.

In raw water sources for domestic use, state and regional agencies generally specify that suspended solids in streams shall not be present in sufficient concentration to be objectionable or to interfere with normal treatment processes. Suspended solids in water may interfere with many industrial processes, and cause foaming in boilers, or encrustations on equipment exposed to water, especially as the temperature rises. Suspended solids are undesirable in water for textile industries, paper and pulp, beverages, dairy products, laundries, dyeing, photography, cooling systems and power plants. Suspended particles also serve as a transport mechanism for pesticides and other substances which are readily sorbed into or onto clay particles.

Solids may be suspended in water for a time and then settle to the bed of the stream or lake. These settleable solids discharged with man's wastes may be inert, slowly biodegradable materials, or rapidly decomposable substances. While in suspension, they increase the turbidity of the water, reduce light penetration and impair the photosynthetic activity of aquatic plants.

Solids in suspension are esthetically displeasing. When they settle to form sludge deposits on the stream or lake bed they are often much more damaging to the life in water, and they retain the capacity to displease the senses. Solids, when transformed to sludge deposits, may do a variety of damaging things, including blanketing the stream or lake bed and thereby destroying the living spaces for those benthic organisms that would otherwise occupy the habitat. Organic solids of a decomposable nature use a portion or all of the dissolved oxygen available in the area. Organic materials also serve as a seemingly inexhaustible food source for sludgeworms and associated organisms.

Turbidity is principally a measure of the light absorbing properties of suspended solids. It is frequently used as a substitute method of quickly estimating the total suspended solids when the concentration is relatively low.

PHOSPHORUS

During the past 30 years, a formidable case has developed for the belief that increasing standing crops of aquatic plant growths, which often interfere with water uses and are nuisances to man, frequently are caused by increasing supplies of phosphorus. Such phenomena are associated with a condition of accelerated eutrophication or aging of waters. It is generally recognized that phosphorus is not the sole cause of eutrophication, but there is evidence to substantiate that it is frequently the key element in all of the elements required by fresh water plants and is generally present in the least amount relative to need. Therefore, an increase in phosphorus allows use of other, already present, nutrients for plant growths. Phosphorus is usually described, for this reason, as a "limiting factor."

When a plant population is stimulated in production and attains a nuisance status, a large number of associated liabilities are immediately apparent. Dense populations of pond weeds make swimming dangerous. Boating and water skiing and sometimes fishing may be eliminated because of the mass of vegetation that serves as a physical impediment to those activities. Plant populations have been associated with stunted fish populations and with poor fishing. Plant nuisances emit vile stenches, impart tastes and odors to water supplies, reduce the efficiency of industrial and municipal water treatment, impair beauty, reduce or restrict resort trade, lower waterfront property values, cause skin rashes to man during water contact, and serve as a desired substrate and breeding ground for flies.

Phosphorus in the elemental form is particularly toxic, and subject to bioaccumulation in much the same way as mercury. Colloidal elemental phosphorus will poison marine fish (causing skin tissue breakdown and discoloration). Also, phosphorus is capable of being concentrated and will accumulate in organs and soft tissues. Experiments have shown that marine fish will concentrate phosphorus from water containing as little as 1 ug/l.

SULFATES AND SULFITES

Sulfites are oxidized to sulfates in streams, exerting a chemical oxygen demand on the streams.

Sulfates are not particularly harmful, but are a major constituent of the total dissolved solids in waste waters from this industry (and are discussed separately as such).

FLUORIDES

As the most reactive non-metal, fluorine is never found free in nature. It is a constituent of fluorite or fluorspar (calcium fluoride) in sedimentary rocks and of cryolite (sodium aluminum fluoride) in igneous rocks. Owing to their origin only in certain types of rocks and only in a few regions, fluorides in high concentrations are not a common constituent of natural surface waters, but they may occur in detrimental concentrations in ground waters.

Fluorides are used as insecticides, for disinfecting brewery apparatus, as a flux in the manufacture of steel, for preserving wood and mucilages, for the manufacture of glass and enamels, in chemical industries, for water treatment, and for other uses.

Fluorides in sufficient quantity are toxic to humans, with doses of 250 to 450 mg giving severe symptoms or causing death.

There are numerous articles describing the effects of fluoride-bearing waters on dental enamel of children; these studies lead to the generalization that water containing less than 0.9 to 1.0 mg/l of fluoride will seldom cause mottled enamel in children, and for adults, concentrations less than 3 or 4 mg/l are not likely to cause endemic cumulative fluorosis and skeletal effects. Abundant literature is also available describing the advantages of maintaining 0.8 to 1.5 mg/l of fluoride ion in drinking water to aid in the reduction of dental decay, especially among children.

Chronic fluoride poisoning of livestock has been observed in areas where water contained 10 to 15 mg/l fluoride. Concentrations of 30 - 50 mg/l of fluoride in the total ration of dairy cows is considered the upper safe limit. Fluoride from waters apparently does not accumulate in soft tissue to a significant degree and it is transferred to a very small extent into the milk and to a somewhat greater degree into eggs. Data for fresh water indicate that fluorides are toxic to fish at concentrations higher than 1.5 mg/l.

CHLORIDE

Dissolved chlorides are a major constituent of the total dissolved solids in waste waters from this industry (and are discussed separately as such).

Sodium and calcium chlorides are found naturally in unpolluted waters, but are harmful to fish in high concentrations.

The natural salinity of river water in the Chesapeake Estuary is 9.5 to 11.0 mg/l of chloride; and the natural salinity of ocean water is 7,000 to 10,300 mg/l of chloride.

DISSOLVED SOLIDS

In natural waters the dissolved solids consist mainly of carbonates, chlorides, sulfates, phosphates, and possibly nitrates of calcium, magnesium, sodium, and potassium, with traces of iron, manganese and other substances.

Many communities in the United States and in other countries use water supplies containing 2000 to 4000 mg/l of dissolved salts, when no better water is available. Such waters are not palatable, may not quench thirst, and may have a laxative action on new users. Waters containing more than 4000 mg/l of total salts are generally considered unfit for human use, although in hot climates such higher salt concentrations can be tolerated whereas they could not be in temperate climates. Waters containing 5000 mg/l or more are reported to be bitter and act as bladder and intestinal irritants. It is generally agreed that the salt concentration of good, palatable water should not exceed 500 mg/l.

Limiting concentrations of dissolved solids for fresh water fish may range from 5,000 to 10,000 mg/l, according to species and prior acclimatization. Some fish are adapted to living in more saline waters, and a few species of fresh water forms have been found in natural waters with a salt concentration of 15,000 to 20,000 mg/l. Fish can slowly become acclimatized to higher salinities, but fish in waters of low salinity cannot survive sudden exposure to high salinities, such as those resulting from discharges of oil well brines. Dissolved solids may influence the toxicity of heavy metals and organic compounds to fish and other aquatic life, primarily because of the antagonistic effect of hardness on metals.

Waters with total dissolved solids over 500 mg/l have decreasing utility as irrigation water. At 5,000 mg/l water has little or no value for irrigation.

Dissolved solids in industrial waters can cause foaming in boilers and cause interference with cleaness, color, or taste of many finished products. High contents of dissolved solids also tend to accelerate corrosion.

Specific conductance is a measure of the capacity of water to convey an electric current. This property is related to the total concentration of ionized substances in water and water temperature. This property is frequently used in a substitute method of quickly estimating the dissolved soldids concentration.

pH, ACIDITY AND ALKALINITY

Acidity is produced by substances that yield hydrogen ions on hydrolysis and alkalinity is produced by substances that yield hydroxyl ions. The terms "total acidity" and "total alkalinity" are often used to express the buffering capacity of a solution. Acidity in natural waters is caused by carbon dioxide, mineral acids, weakly dissociated acids, and the salts of strong acids and weak bases. Alkalinity is caused by strong bases and the salts of strong alkalies and weak acids.

The term pH is a logarithmic expression of the concentration of hydrogen ions. At a pH of 7, the hydrogen and hydroxyl ion concentrations are essentially equal and the water is neutral. Lower pH values indicate acidity while higher values indicate alkalinity. The relationship between pH and acidity or alkalinity is not necessarily linear or direct.

Waters with a pH below 6.0 are corrosive to water works structures, distribution lines, and household plumbing fixtures and can thus add such constituents to drinking water as iron, copper, zinc, cadmium and lead. The hydrogen ion concentration can affect the taste of the water. At a low pH water tastes sour. The bactericidal effect of chlorine is weakened as the pH increases, and it is advantageous to keep the pH close to 7. This fact is very significant for providing safe drinking water.

Extremes of pH or rapid pH changes can exert stress or kill aquatic life outright. Dead fish, associated algal blooms, and foul stenches are esthetic liabilities to any waterway. Even moderate changes from "acceptable" criteria limits of pH are deleterious to some species. The relative toxicity to aquatic life of many materials is increased by changes in the water pH. Metalocyanide complexes can increase a thousandfold in toxicity with a drop of 1.5 pH units. The availability of many nutrient substances varies with the alkalinity and acidity. Ammonia is more lethal with a higher pH.

The lacrimal fluid of the human eye has a pH of approximately 7.0, and a deviation of 0.1 pH unit from the norm may result in eye irritation for the swimmer. Enough irritation will cause severe pain.

TEMPERATURE

Temperature is one of the most important and influential water quality characteristics. Temperature determines those species that may be present; it activates the hatching of young, regulates their activity, and stimulates or suppresses their growth and development; it attracts, and may kill when the water becomes too hot or becomes chilled too suddenly. Colder water generally suppresses development; warmer water generally accelerates activity and may be a primary cause of aquatic plant nuisances when other environmental factors are suitable.

Temperature is a prime regulator of natural processes within the water environment. It governs physiological functions in organisms and, acting directly or indirectly in combination with other water quality constituents, it affects aquatic life with each change. These effects include chemical reaction rates, enzymatic functions, molecular movements, and molecular exchanges between membranes within and between the physiological systems and the organs of an animal.

Chemical reaction rates vary with temperature and generally increase as the temperature is increased. The solubility of gases in water varies with temperature. Dissolved oxygen is decreased by the decay or decomposition of dissolved organic substances and the decay rate increases as the temperature of the water increases, reaching a maximum at about 30°C (86°F). The temperature of stream water, even during summer, is below the optimum for pollution-associated bacteria. Increasing the water temperature increases the bacterial multiplication rate when the environment is favorable and the food supply is abundant.

Reproduction cycles may be changed significantly by increased temperature because this function takes place under restricted temperature ranges. Spawning may not occur at all because temperatures are too high. Thus, a fish population may exist in a heated area only by continued immigration. Disregarding the decreased reproductive potential, water temperatures need not reach lethal levels to destroy a species. Temperatures that favor competitors, predators, parasites, and disease can destroy a species at levels far below those that are lethal.

Fish food organisms are altered severely when temperatures approach or exceed 90°F. Predominant algal species change, primary production is decreased, and bottom associated organisms may be depleted or altered drastically in numbers and distribution. Increased water temperatures may cause aquatic plant nuisances when other environmental factors are favorable.

Synergistic actions of pollutants are more severe at higher water temperatures. Given amounts of domestic sewage, refinery wastes, oils, tars, insecticides, detergents, and fertilizers more rapidly deplete oxygen in water at higher temperatures, and the respective toxicities are likewise increased.

When water temperatures increase, the predominant algal species may change from diatoms to green algae, and finally at high temperatures to blue-green algae, because of species temperature preferentials. Blue-green algae can cause serious odor problems. The number and distribution of benthic organisms decrease as water temperatures increase above 90°F, which is close to the tolerance limit for the population. This occurrence could seriously affect certain fish that depend on benthinc organisms as a food source.

The cost of fish being attracted to heated water in winter months may be considerable, due to fish mortalities that may result when the fish return to the cooler water.

Rising temperatures stimulate the decomposition of sludge, formation of sludge gas, multiplication of saprophytic bacteria and fungi (particularly in the presence of organic wastes), and the consumption of oxygen by putrefactive processes, thus affecting the esthetic value of a watercourse.

In general, marine water temperatures do not change as rapidly or range as widely as those of fresh waters. Marine and estuarine fishes, therefore, are less tolerant of temperature variation. Although this limited tolerance is greater in estuarine than in open water marine species, temperature changes are more important to those fishes in estuaries and bays than to those in open marine areas, because of the nursery and replenishment functions of the estuary that can be adversely affected by extreme temperature changes.

ARSENIC

Arsenic is found to a small extent in nature in the elemental form. It occurs mostly in the form of arsenites of metals or as pyrites.

Arsenic is normally present in seawater at concentrations of 2 to 3 ug/l and tends to be accumulated by oysters and other shellfish. Concentrations of 100 mg/kg have been reported in certain shellfish. Arsenic is a cumulative poison with long-term chronic effects on both aquatic organisms and mammalian species, and a succession of small doses may add up to a final lethal dose. It is moderately toxic to plants and highly toxic to animals especially as AsH_3.

Arsenic trioxide, which also is exceedingly toxic, was studied in concentrations of 1.96 to 40 mg/l and found to be harmful in that range to fish and other aquatic life. Work by the Washington Department of Fisheries on pink salmon has shown that a level of 5.3 mg/l of As_2O_3 for 8 days was extremely harmful to this species; on mussels, a level of 16 mg/l was lethal in 3 to 16 days.

Severe human poisoning can result from 100 mg concentrations, and 130 mg has proved fatal. Arsenic can accumulate in the body faster than it is excreted and can build to toxic levels from small amounts taken periodically through lung and intestinal walls from the air, water and food.

Arsenic is a normal constituent of most soils, with concentrations ranging up to 500 mg/kg. Although very low concentrations of arsenates may actually stimulate plant growth, the presence of excessive soluble arsenic in irrigation waters will reduce the yield of crops, the main effect appearing to be the destruction of chlorophyll in the foliage. Plants grown in water containing one mg/l of arsenic trioxides showed a blackening of the vascular bundles in the leaves. Beans and cucumbers are very sensitive, while turnips, cereals, and grasses are relatively resistant. Old orchard soils in Washington that contained 4 to 12 mg/kg of arsenic trioxide in the top soil were found to have become unproductive.

VANADIUM

Metallic vanadium does not occur free in nature, but minerals containing vanadium are widespread. Vanadium is found in many soils and occurs in vegetation grown in them. Vanadium adversely effects some plants in concentrations as low as 10 mg/l.

Vanadium as calcium vanadate can inhibit the growth of chicks, and in combination with selenium increases mortality in rats. Vanadium appears to inhibit the synthesis of cholesterol and accelerate its catabolism in rabbits.

Vanadium causes death to cccur in fish at low concentrations. The amount needed for lethality depends on the alkalinity of the water and the specific vanadium compound present. The common bluegill can be killed by about 6 ppm in soft water and 55 ppm in hard water when the vanadium is expressed as vanadryl sulfate. Other fish are similarly affected.

Specific conductance is a measure of the capacity of water to convey an electric current. This property is related to the total concentration of ionized substances in water and water temperature. This property is frequently used as a substitute method of quickly estimating the dissolved solids concentration.

CADMIUM

Cadmium in drinkino water supplies is extremely hazardous to humans, and conventional treatment as practiced in the United States does not remove it. Cadmium is cumulative in the liver, kidney, pancreas, and thyroid of humans and other animals. A severe bone and kidney syndrome in Japan has been associated with the ingestion of as little as 600 ug/day of cadmium.

Cadmium is an extremely dangerous cumulative toxicant, causing insidious progressive chronic poisoning in mammals, fish, and probably other animals because the metal is not excreted. Cadmium could form organic compounds which might lead to mutagenic or teratogenic effects. Cadmium is known to have marked acute and chronic effects on aquatic organisms also.

Cadmium acts synergistically with other metals. Copper and zinc substantially increase its toxicity. Cadmium is concentrated by marine organisms, particularly molluscs, which accumulate cadmium in calcareous tissues and in the viscera. A concentration factor of 1000 for cadmium in fish muscle has been reported, as have concentration factors of 3000 in marine plants, and up to 29,600 in certain marine animals. The eggs and larvae of fish are apparently more sensitive than adult fish to poisoning by cadmium, and crustaceans appear to be more sensitive than fish eggs and larvae.

RADIOACTIVITY

Ionizing radiation, when absorbed in living tissue in quantities substantially above that of natural background levels, is recognized as injurious. It is necessary, therefore, to prevent excessive levels of radiation from reaching any living organism:

humans, fishes, and invertebrates. Beyond the obvious fact that including they emit ionizing radiation, radioactive wastes are similar in many respects to other chemical wastes. Man's senses cannot detect radiation unless it is present in massive amounts. Plants and animals, to be of any significance in the cycling of radionuclides in the aquatic environment, must accumulate the radionuclide, retain it, be eaten by another organism, and be digestible. However, even if an organism accumulates and retains a radionuclide and is not eaten before it dies, the radionuclide will enter the "biological cycle" through organisms that decompose the dead organic material into its elemental components. Plants and animals that become radioactive in this biological cycle can thus pose a health hazard when eaten by man.

Aquatic life may receive radiation from radionuclides present in the water and substrate and also from radionuclides that may accumulate within their tissues. Humans can acquire radionuclides through many different pathways. Among the most important are through drinking contaminated water and eating fish and shellfish that have concentrated nuclides from the water. Where fish or other fresh or marine products that have accumulated radioactive materials are used as food by humans, the concentrations of the nuclides in the water must be further restricted, to provide assurance that the total intake of radionuclides from all sources will not exceed the recommended levels.

In order to prevent unacceptable doses of radiation from reaching humans, fish, and other important organisms, the concentrations of radionuclides in water, both fresh and marine, must be restricted.

CONCLUSION

In view of the data presented above, it is judged that all of the mentioned waste constituents generated in the phosphate industry should be identified as pollution parameters as defined in the Federal Water Pollution Control Act Amendments of 1972.

In the paragraphs above, the harmful characteristics are given of all the parameters that are encountered in the phosphate manufacturing point source category. Table 11 summarizes the parameters found for each chemical.

Although many parameters appear in the waste streams from these plants, only those primary parameters signified by "x" need be used to set effluent standards.

The remaining parameters signified by zeros are adequately treated if the primary parameters are so treated.

TABLE 11

WASTE WATER CONSTITUENTS OF PHOSPHATE CATEGORY

Chemical	Parameter										
	TSS	PO_4 PO_3	SO_4 SO_3	F SiF_6	Cl	TDS	low pH	Heat	P_4	As	V, Cd, Ra, U
P_4 & Fe_2P	X	X	0	X		0	0	0	X	0	0
H_3PO_4		0				0	0	0	0	0	
P_2O_5		0				0	0	0	0		
P_2S_5		0	0			0	0	0	0	0	
PCl_3	X	X			0	0	X	0	0	X	
$POCl_3$	X	X			0	0	X	0	0	0	
$Na_5P_3O_{10}$		0				0	0	0	0		
$CaHPO_4$ (feed grade)	X	X		0		0	0	0	0		
$CaHPO_4$ (food grade)	0	0				0	0	0	0		

SECTION VII

CONTROL AND TREATMENT TECHNOLOGY

INTRODUCTION

Section V of this report quantitatively discussed the specific water uses in the phosphate industry and the raw wastes from this industry before control and/or treatment of these wastes. Section VI identified the constituents of the raw wastes which are classified as pollutants. Table 11 summarizes the pollutant constituents found as raw wastes in each of the three segments of the industry.

Two major observations may be made from table 11:

1. Classical sanitary engineering practices that treat effluents containing organic material or that are aimed at reducing biological oxygen demand are inapplicable to the phosphate manufacturing industry, where such pollutant constituents are usually very low and not a significant factor. Hence, control and treatment of the wastes in this industry are of the chemical and chemical engineering variety, and include neutralization, pH control, precipitation, ionic reactions, filtration, centrifugation, ion exchange, demineralization, evaporation and drying.

2. A limited number of pollutant constituents characterizes the entire industry, crossing the lines between segments of the industry. Hence, the control and treatment techniques should be similar throughout the industry.

In this section of the report, the control and treatment technology is discussed in considerable detail. Much of this discussion is based on observed actual abatement practice in the industry and the accomplishments of independently verified sampling data of plant effluents.

IN-PROCESS CONTROLS

Control of the wastes includes in-process abatement measures, monitoring techniques, safety practices, housekeeping, containment provisions and segregation practices.

Segregation of Water Streams

Probably the most important waste control technique, particularly for subsequent treatment feasibility and economics, is segregation.

Incoming pure water picks up contaminants from various uses and sources including:

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1. non-contact cooling water
2. contact cooling water
3. process water
4. washings, leaks and spills
5. incoming water treatments
6. cooling tower blowdowns
7. boiler blowdowns

If wastes from these sources are segregated logically, their treatment and disposal may sometimes be eliminated entirely through use in other processes or recycle. In many instances, the treatment costs, complexity and energy requirements may be significantly reduced. Unfortunately, it is a common practice today to blend small, heavily contaminated streams with large non-contaminated streams such as cooling water effluents. Once this has been allowed to happen, treatment costs, energy requirements for these treatments, and the efficient use of water resources have all been compromised.

In general, plant effluents can be segregated into:

1. Non-contaminated Cooling Water. Except for leaks, non-contact water has no waste pickup. It is usually high volume.

2. Process Water. Usually contaminated but often small volume.

3. Auxiliary Streams. Ion exchange regenerants, cooling tower blowdowns, boiler blowdowns, leaks, washings - low volume but often highly contaminated.

Although situations vary, the basic segregation principle is don't mix large uncontaminated cooling water streams with a smaller contaminated process and auxiliary streams before full treatment and/or disposal. It is almost always easier and more economical to treat and dispose of the small volumes of waste effluents - capital costs, energy requirements, and operating costs are all lower.

In the phosphorus chemicals industry, many plants have accomplished the desired segregation of water streams, often by a painstaking rerouting of sewer lines which have existed for many years. Among these plants which are notable in this respect are Plants 003, 037, 042, 075, and 182.

Recycle of Scrubber Water

The widespread use of water for scrubbing of tail gases in this industry has unfortunately led to many examples where the use of once-through scrubber water is the method of operation. However, there are several plants notable in this respect which recycle scrubber water from a sump, thus satisfying the scrubber water flow rate demands (on the basis of mass transfer considerations) while retaining control of water usage. These notable plants are TVA (Muscle Shoals, Alabama), and Plants 003 and 182.

Recycle of scrubber water permits the subsequent treatment of much smaller quantities of waste water with much higher concentrations of polluting constituents. Both these attributes make waste water treatment more economical, and in some cases, more efficient, from a removal viewpoint.

Dry Dust Collection

A drastic reduction in the aqueous waste load may be made by replacing wet scrubbing systems with baghouses, or alternatively, by placing cyclone dust collectors upstream of wet scrubbers. This approach is feasible because baghouses have recently been improved in design to the point where operation and maintenance costs are not excessive, where solids collection efficiences exceed those of wet scrubbers, and where operating temperature ranges have been extended with high-temperature media development. Dry collected solids may be returned to the product stream, provided that a separate collector is installed for each product. This is a change in approach for the typical multiproduct phosphate plant, since conventional practice has been to centralize the collection and treatment functions across product lines. With dry separate collection, the product recovered may significantly contribute to alleviating the operating cost of the collectors.

Plants in this industry which are notable in this respect in having at least some dry dust collection include Plants 003, 006, 042, 119, and 182.

Housekeeping and Containment

Containment and disposal requirements may be divided into several categories:

1. minor product spills and leaks
2. major product spills and leaks
3. upsets and disposal failures
4. storm water runoff
5. pond failures
6. vessel and container cleanout

Minor Spills and Leaks

There are minor spills and leaks in all industrial chemical manufacturing operations. Pump seals leak, hoses drip, equipment is washed down, pipes and equipment leak, valves drip, tank leaks occur, solids spill and so on. These losses are not going to be eliminated. They can be minimized and contained. In some cases the products are valuable; in other cases, personnel safety and prevention of corrosion may be paramount.

Reduction techniques are mainly good housekeeping and attention to sound engineering and maintenance practices. Pump seals or types of pumps are changed. Valves are selected for minimizing drips. Pipe and equipment leaks are minimized by selection of corrosion-resistant materials.

Containment techniques employ the use of drip pans under pumps, valves, critical small tanks or equipment, and known leak and drip areas such as loading or unloading stations. Solids can be cleaned up or washed down. All of these minor leaks and spills should then go to a containment system, catch basin, sump pump or other area that collects and isolates all of them from other water systems. They should go from this system to suitable treatment facilities.

Of special importance in the phosphorus consuming subcategory of the industry is the containment of phossy water from phosphorus transfer and storage operations. While displaced phossy water is normally shipped back to the phosphorus-producing facility, current practice in phosphorus storage tanks is to maintain a water blanket over the phosphorus for safety reasons. Make-up water is added resulting in the overflow of excess water.

This method of level control is unacceptable since it results in the discharge of phossy water. One way to ensure zero discharge is to install an auxiliary tank to collect phossy water overflows from the phosphorus storage tank; this system can be closed-loop by reusing this phossy water from the auxiliary tank as make-up for the main phosphorus tank. This scheme preserves the positive safety features of the existing level control practice and also safeguards against inadvertent large discharges resulting from leaky or misadjusted water make-up valves.

Major Product Spills and Leaks

These are catastrophic occurrences with major loss of product, tank and pipe ruptures, open valves, explosions, fires, and earthquakes.

No one can predict, plan for, or totally avoid these happenings, but they are extremely rare. Probably the most common of these rare occurrences is tank or valve failures. These can be handled with adequate dikes able to contain the tank volume. All acid, caustic, or toxic material tanks should be diked to provide this protection. Other special precautions may be needed for flammable or explosive substances. Plant 037 is a prime example where product tanks and transfer pumps have been systematically diked for containment of spills.

Upsets and Disposal Failures

In many processes there are short term upsets. These may occur during startup or shutdown or during normal operation. The phosphorus consuming subcategory and the phosphate subcategory of this industry may be more vulnerable to this type of upset since so many of the processes are batch-type operations with much more direct operator control then the large-scale automated continuous processes typically found in the chemical industry.

These upsets represent a small portion of overall production but they nevertheless contribute to waste loads. The upset products should be treated, separated, and largely recycled. In the event that this can not be done, they must be disposed of.

One very special problem in the phosphorus consuming subcategory is the inadvertent spill of elemental phosphorus into a plant sewer line. Past practice has been to let it remain in the sewer and ensure a continuous water flow to prevent fire. There has been general reluctance to clean it out since phosphorus burns when exposed to air. With this practice, of course, all water flowing in that sewer from that time on becomes contaminated with phosphorus.

Provisions can be made for collecting, segregating and bypassing such phosphorus spills. One method is the installation of a trap of sufficient volume just downstream of reaction vessels, with appropriate installations and valving to enable the bypass of that trap after a spill has occurred and the offline removal and cleaning of the trap (with safe disposal of the phosphorus).

Stormwater Runoff

The phosphates segment of this industry is characterized by the handling, storing, conveying, sizing, packaging and shipping of finely-divided solid products. Typically, a phosphate plant has all the exterior surface of buildings, equipment and grounds covered with dusts. An area of concern is the pickup of these solids by stormwater either as suspended solids or as dissolved solids. Of course, washing down of these dusts is not acceptable; the dry solids must be collected. Where possible, the solids may be returned to appropriate process streams. Where purity requirements prohibit this return, adequate means for safe disposal of solid wastes must be provided.

Plants 003, 042 and 182 are examples of plants which have positive continual cleanup programs for solids, which minimize stormwater runoff. Most plants (with considerable credit to air pollution abatement practices) have also minimized the quality of airborne dusts.

The very practice of process water segregation discussed previously has led to the direct discharge of stormwater without treatment. Little is known from a quantitative standpoint about the severity of this problem in the phosphates segment of the industry, or to what extent containment and treatment of stormwater is required. In the phosphorus manufacturing segment of the industry, where large quantities of dusts are handled, Plant 159 collects approximately 10 kg/kkg (20 lb/ton) in a settling pond for stormwater and non-contact cooling water.

Pond Failures

Unlined ponds are the most common treatment facility used by the industry. Failures of such ponds occur because they are unlined and because they are improperly constructed for containment in times of heavy rainfall.

Unlined ponds may give good effluent control if dug in impervious clay areas or poor control if in porous, sandy soil. The porous ponds will allow effluent to diffuse into the surrounding earth and water streams. This may or may not be detrimental to the area, but it is certainly poor waste control. Lined ponds are the only answer in these circumstances.

Many ponds used today are large low-diked basins. In times of heavy rainfall, much of the pond content is released into either the surrounding countryside, or, more likely, the nearest body of water. Again, whether this discharge is harmful or not depends on the effluent and the surrounding area, but it does represent poor effluent control.

Good effluent control may be gained by a number of methods, including:

1. Pond and diking should be designed to take the anticipated rainfall; smaller and deeper ponds should be used where feasible.
2. Control ponds should be constructed so that drainage from the surrounding area does not innundate the pond and overwhelm it.
3. Substitution of smaller volume (and surfaced) treatment tanks, coagulators, or clarifiers can reduce rainfall influx and leakage problems.

Vessel and Container Cleanout

One common characteristic of the phosphorus consuming subcategory of the industry is the planned accumulation of residues in reaction vessels and stills, with infrequent shutdowns to clean and remove these residues. In many cases, the residues are washed down with firehoses and the wastes discharged. This practice is clearly unacceptable. One alternative is the diking of the area with collection and treatment of the aqueous wastes, in conjunction with an effort to minimize the quantity of washwater.

A similar situation exists with regard to the cleaning of returnable containers (drums, tank trucks and tank cars) before reuse. Since these are routine operations, procedures and facilities must be made available for minimizing the quantity of waste water and for the collection and treatment of this waste water.

Monitoring Techniques

Since the chemical process industry is among the leaders in instrumentation practices and application of analytical techniques to process monitoring and control, there is rarely any problem in finding technology applicable to waste water analysis. Acidity and alkalinity are detected by pH meters, often installed in-line for continuous monitoring and control.

Dissolved solids may be estimated by conductivity measurements, suspended solids and turbidity and specific ions by wet chemistry and colorimetric measurements. Flow meters of numerous varieties are available for measuring flow rates.

The pH meter is the most commonly used in-line monitoring instrument. Spills, washdowns and other contributions become quickly evident. Alarms set off by sudden pH changes alert the operators and often lead to immediate plant shutdowns or switching effluent to emergency ponds for neutralization and disposal. Use of in-line pH meters will be given additional coverage in the control and treatment sections for specific chemicals.

Monitoring and control of harmful materials such as phosphorus and arsenic is often so critical that batch techniques may be used. Each batch can be analyzed before discharging. This approach provides absolute control of all wastes passing through the system. Unless the process is unusually critical, dissolved solids are not monitored continuously. This follows from the fact that most dissolved solids are rather inert. Chemical analyses on grab or composite effluent samples are commonly used to establish total dissolved solids, chlorides, sulfates, and other low ion concentrations.

Summary

The preceding narrative described general treatment practices and in-plant controls. The following discusses specific abatement measures recommended for each subcategory.

TREATMENT OF WASTE WATERS IN THE PHOSPHORUS SUBCATEGORY

Neutralization of Acidic Waste waters

Virtually every manufacturing process in the phosphate industry results in a raw waste load of significant acidity. In some cases, advantage is taken of the availability of alkaline waste to at least partially neutralize the acid waste streams.

At phosphorus producing plants, some neutralization of acidic calciner scrubber liquor is achieved by the alkaline slag or by the slightly alkaline slag quench liquor (see Table 7). At TVA, the slag is granulated by quenching with a high-velocity jet of calciner scrubber liquor plus process cooling water. The granulated slag (with its large surface area) effectively neutralizes the acidic liquors. At plants not granulating slag (Plants 028 and 181), the slightly alkaline slag quench liquors are mixed with the highly acidic scrubber liquors for partial neutralization.

Except for this one case where granulated slag is available, lime or limestone neutralization of acid waste streams is standard practice in this industry as observed at Plants 003, 006, 028, 159, 181, and 182. The relative chemical costs reported by Downing, Kunin and Polliot(28), listed in Table 12, show that limestone or lime are far and away more economical than other neutralizing materials. Limestone is the lower cost material (approximately $11/kkg ($10/ton)) but suffers the disadvantages of slower reaction and lower obtainable pH than lime. Lime costs approximately $22/kkg ($20/ton).

With the exception of hydrochloric acid from PCl_3 and $POCl_3$ manufacturing facilities, every acid waste in the phosphorus chemicals industry forms insoluble or slightly soluble calcium salts when treated with lime:

Acid	Calcium Salt	Solubility*, mg/l
H_3PO_4	$Ca(H_2PO_4)_2.H_2O$, MCP	18,000
"	$CaHPO_4.2H_2O$, DCP	200
"	$Ca_3(PO_4)_2$, TCP	25
HF, H_2SiF_6	CaF_2	16
H_2SiO_3	$CaSiO_3$	95
H_2SO_4	$CaSO_4.2H_2O$	2,410
H_2SO_3	$CaSO_3.2H_2O$	43
H_3PO_3	$2\ CaHPO_3.3H_2O$	(Slightly Soluble)

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*Between 17°C and 30°C.

It is readily apparent that lime treatment (with excess lime) not only neutralizes acidic waste waters from the phosphate manufacturing industry, but also demineralizes most waste waters by precipitating calcium salts. This then produces a solid waste which may be disposed of by landfilling.

TABLE 12 Relative Chemical Costs for Neutralizing Acid Wastes
Source: Downing, Kunin and Polliot(28)

NEUTRALIZING MATERIAL	Relative Cost per Pound Alkali*	Relative Weight Alkali Required Per Pound Acid			Relative Cost Per Pound Acid		
		H_2SO_4	HCl	H_3PO_4	H_2SO_4	HCl	H_3PO_4
Lump limestone, high Ca	1.16	110	148	165	128	172	191
Lump limestone, dolomitic	1.00	94	127	141	94	127	141
Pulv. limestone, high Ca	1.59	110	148	165	175	235	262
Pulv. limestone, dolomitic	1.37	94	127	141	129	174	193
Hydrated lime, high Ca	3.06	79	107	119	242	327	364
Hydrated lime, dolomitic	2.50	65	87	98	162	217	245
Pebble lime, high Ca	2.07	60	80	90	124	166	186
Pebble lime, dolomitic	1.87	54	73	81	101	136	151
Pulv. quicklime, high Ca	2.18	60	80	90	131	174	196
Pulv. quicklime, dolomitic	1.97	54	73	81	106	144	159
Sodium bicarbonate	20.65	173	233	260	3570	4810	5360
Soda ash	13.08	119	160	179	1560	2090	2340
Caustic soda (50%)	9.96	164	220	246	1630	2190	2450
Ammonia (anhyd.)	5.90	35	47	53	207	277	313
Magnesium oxide	3.90	42	56	63	164	218	246

*Delivered cost including freight.

The effectiveness of the control specified in the preceding paragraphs is summarized in Table 13 for four plants (TVA, 181, 028 and 159). Data for plants 028 and 159 were taken from Tables 14 and 15, which include a complete analysis on the intake and effluent waters.

Removal of Anions (Except Chlorides) From Acidic Wastes

Neutralization of acid waste waters with lime also precipitates the calcium salts of all acid wastes in this industry (with the exception of hydrochloric acid from PCl_3 and $POCl_3$ manufacture). This treatment is widespread throughout the phosphate manufacturing industry, and represents a class of treatment technology which has widespread validation and demonstration at plant-scale installations.

Other technologies for removing dissolved solids (except chlorides) are also presented in this section, with a somewhat lesser degree of full-scale validation than lime treatment.

Treatment of Acidic Fluoride Wastes

Acidic fluoride wastes are generated by the phosphorus producsegment of the industry and by the defluorination of wet-process acid in the manufacture of animal feed grade calcium phosphates. These waste waters containing large quantities of hydrofluoric, fluosilicic and silicic acids are neutralized with lime (which breaks down H_2SiF_6 at high pH) to precipitate calcium fluoride and gelatinous hydrated silica. Lime treatment is standard operating technology at Plants 128, 159, 181 and 182.

Like lime treatment of phosphoric acid, lime treatment of acidic fluoride wastes is enhanced by the decreased solubility of CaF_2 at high pH:

$$CaF_2(s) \longrightarrow Ca^{+2} + 2F \xrightarrow{2H_2O} Ca^{+2} + 2OH + 2HF$$

The equilibrium is driven to the far left by the addition of excess lime. The theoretical solubility of CaF_2 may be calcined in much the same manner as outlined for $Ca_3(PO_4)_2$, using the ionization constant of HF and the pure water solubility data for CaF_2.

There has been recent commercial interest in recovering the fluoride values in acidic waste waters. Two commercial processes have been developed to manufacture hydrofluoric acid and one to manufacture synthetic cryolite for the aluminum industry.

Removal of Suspended Solids

The raw waste streams from the phosphorus producing segment and from the phosphate subcategory of the industry contain considerable quantities of suspended solids. Moreover, the

TABLE 13 Summary of Control & Treatment Techniques at Phosphorus-Producing Plants
(For Process Waters Other Than Phossy Water)

	TSS	Total Acidity (Alkal-inity)	TDS	Fluoride	Sulfate	Total Phosphate
Raw Waste Loads (from Sec. V)						
Kg/Kkg	42.5	54.5	-	53.5	111	25
lb /ton	85	109	-	107	222	50
Waste Discharged, Kg/Kkg:						
TVA	0	0	0	0	0	0
Plant 181	0	0	0	0	0	0
Plant 028 (Net)	0.5	1	4	0.1	2	0.2
Plant 159 (Gross)	0.5	(12)	22	0.04	3	0.8
Waste Discharged, lb /ton:						
TVA	0	0	0	0	0	0
Plant 181	0	0	0	0	0	0
Plant 028 (Net)	1	3	9	0.2	4	0.4
Plant 159 (Gross)	1	(24)	45	0.07	7	1.6
Control & Treatment Efficiency, Per Cent:						
TVA	100	100	100	100	100	100
Plant 181	100	100	100	100	100	100
Plant 028	99	-	-	99+	98	99
Plant 159	99	-	-	99+	97	97

TABLE 14 - Effluent from Plant 028 (Discharge No. 001)

Effluent Flowrate = 103-200 l/kkg (24,700 gal/ton)

Notes:
1. This Discharge is from Cooling Water and Dust Collector Water.
2. There is Zero Discharge of Phossy Water and Calciner Scrubber Water

	Water & Wastewater Analysis				Net Effluent Qty Kg/Kkg		Net Effluent Qty Lb /ton	
Constituent	Units	Intake	Effluent Plant Data	Effluent Ind. Data	Plant Data	Independent Data	Plant Data	Independent Data
pH	-	-	7.3-9.5	7.55	-	-	-	-
Turbidity	FTU	26	32	30	-	-	-	-
Conductivity	$\frac{\mu mhos}{cm}$	359	403	300	-	-	-	-
TSS	mg/l	15	15	20	-	0.5	0	1
TDS	mg/l	160	202	176	4	2	9	3
$CaCO_3$ Alkalinity	mg/l	116	110	130	(-1)	1	(-1)	3
$CaCO_3$ Acidity	mg/l	-	-	-	-	-	-	-
Chloride	mg/l	<0.1	4.1	8	0.4	0.8	0.9	1.6
Fluoride	mg/l	0.19	1.14	0.87	0.10	0.07	0.20	0.14
Sulfate	mg/l SO_4	6.4	13.8	26	0.8	2.1	1.5	4.1
COD	mg/l	2.0	53.5	25	5.3	2.4	10.6	4.8
Total Hardness	mg/l	116.7	129.7	160	1	4	3	8
Total Phosphate	mg/l PO_4	1.2	2.4	-	0.12	-	0.25	-
Ortho Phosphate	mg/l PO_4	1.2	2.4	2.9	0.12	0.18	0.25	0.35

TABLE **15** Effluent from Plant 159

Notes: 1. There is Zero Discharge of Phossy Water
2. These data are Plant Data, Not Independently Verified

Effluent Flowrate = 36,100 l/kkg (8,640 gal/ton)

Constituent	Units	Water & Wastewater Analysis		Gross Effluent Quantity		Net Effluent Quantity	
		Treated Intake	Effluent	Kg/kkg	lb /ton	Kg/kkg	lb /ton
pH	-	7.5	8.0-8.5	-	-	-	-
Turbidity	FTU	<1	11	-	-	-	-
Conductivity	µmhos/cm	966	898	-	-	-	-
TSS	mg/l	11	15	0.54	1.08	0.14	0.29
TDS	mg/l	617	620	22.4	44.8	0.11	0.22
$CaCO_3$ Alkalinity	mg/l	358	323	11.7	23.4	(-1.3)	(-2.6)
$CaCO_3$ Acidity	mg/l	-	-	-	-	-	-
Chloride	mg/l	50	53	1.9	3.8	0.11	0.22
Fluoride	mg/l	0.84	1.01	0.04	0.07	0.0061	0.0122
Sulfate	mg/l SO_4	91.5	90.0	3.2	6.5	(-0.054)	(-0.108)
COD	mg/l	-	6	-	0.2	0.22	0.43
Total Hardness	mg/l	465	468	16.9	33.8	0.11	0.22
Total Phosphate	mg/l PO_4	18.0	22.4	0.8	1.6	0.16	0.32
Ortho Phosphate	mg/l PO_4	15.9	19.3	0.7	1.4	0.12	0.24

chemical treatment of acidic wastes described in the previous section produced in many instances additional suspended solids.

To facilitate settling of suspended solids, large quiet settling ponds and vessels are needed. Settling ponds are the foremost industrial treatment for removing suspended solids. They are in use at Plants 006, 028, 119, 159, 181 and 182. Removal of suspended solids generates a solid waste effluent which must be disposed of by landfilling.

The size and number of settling ponds differ widely depending on the settling functions required. Waste streams with small suspended solids loads and fast settling characteristics can be cleared up in one or two small ponds; others with heavier suspended solids loads and/or slower settling rates may require 5 to 10 large ponds. Most settling ponds are unlined, but the technology exists for lined ponds.

Although not as widely used as settling ponds, tanks and vessels are also employed for removal of suspended solids in the phosphate manufacturing industry. They are in use at TVA (Muscle Shoals, Alabama) and at Plants 003, 006, 028 and 159.

Commercially these units are listed as clarifiers or thickeners depending on whether they are light or heavy duty. They also have internal baffles, compartments, sweeps and other directing and segregating mechanisms to provide more efficient performance. This feature plus the positive containment and control and reduced rainfall influence (smaller area compared to ponds) should lead to increasing use of vessels and tanks in the future, especially where a plant is short of available land for settling ponds.

Filtration equipment, such as plate-and-frame pressure filters, pressure or vacuum leaf filters, rotary vacuum filters, and pressure tubular filters, has been widely used in the chemical and waste treatment field for many years. The batch-type filters find most use in polishing applications to completely remove small quantities of suspended solids, since the labor-intensive blowdown operation is dependent on cake volume. These filtrations are common for collection of undesirable solid wastes, such as arsenic sulfide from food grade phosphoric acid. Continuous rotary vacuum filters find general applicability in dewatering sludges with high concentrations of solids. Sand bed filtration also finds increasingly widespread use.

Filtration is in use at Plants 006, 075 and 119. In general, filtration is not economically attractive for huge quantities of waste water (except for sand bed filtration). It is usually preceded by a gravity thickening operation so that it treats the thickened sludge which is only a small volumetric percentage of the total waste water flow.

Centrifugation, in use at Plant 003 and at the TVA installation, is an alternative means for mechnical dewatering of relatively low flow rate sludges, and has made major recent inroads into the domestic waste water treatment field. The continuous solid-bowl centrifuge, as its name implies, provides for continuous removal of the cake, and its design reaches a compromise between solids recovery and cake dryness. The basket solid-bowl centrifuge, on the other hand, discharges cake intermittently, and the dewatering and cake-drying portions of the cycle may be separately controlled. Perforated-bowl centrifuges are really centrifugal filters. The solid-bowl machines offer the significant advantage over filters that blinding of a medium is removed as a problem area.

Dewatering of Lime-Precipitated Phosphates

Although (as previously discussed) lime can be used to effectively precipitate phosphates from solution to reduce the concentration to 0.3 mg/l or less (as PO$_4$), the lime-precipitated phosphates do not dewater readily, but form a water-trapping gel structure. After 24 hours of settling, clarified effluents still may have 15 to 50 mg/l of suspended solids. This condition can be significantly improved by increasing the detention time to 7 days, but the suspended solids content may still be 5 mg/l or greater. In the phosphate manufacturing industry, settling ponds with 7 days or longer detention times (equivalent to an overflow rate of 420 l/day/m^2 (10 gpd/ft^2) at a nominal depth of 3 m (10 ft)) are used. It has been reported that the settling characteristics are strongly dependent on the initial concentration of phosphate ion. An initial concentration of 75,000 mg/l resulted in a compacted settled slurry density 3 to 5 times higher than if the initial concentration was 1,500 mg/l.

Where sufficient land area for large settling ponds is not available, average removal efficiencies of 80 to 95 percent have been obtained with mechanically raked gravity thickeners. A typical thickener design has a 2-hour detention time and an overflow rate of 42,000 l/day/m^2 (1,000 gpd/ft^2).

Synthetic organic, water-soluble, high molecular weight polyelectrolytes have achieved great success in flocculation and clarification and in sludge conditioning before centrifugation or filtration. A polymer dosage of 0.05 kg per kkg of dry sludge solids (0.1 lb/ton), or about 1 mg/l of a 2 percent slurry, may achieve 85 percent removal of suspended solids at a detention time of 2 hours, with a 12 percent solids content in the thickened sludge. If this thickened sludge were then vacuum filtered, a cake of 30 percent solids could be obtained with a solids content in the filtrate of 0.5 mg/l of less.

The following may be a typical performance chart for an influent sludge containing 100 liters of water:

	Volume of Water, liters	Suspended Solids Kg	Suspended Solids Percentage
Influent	100	2.56	2.5%
Thickener Overflow	84	0.38	0.45%
Thickener Underflow	16	2.18	12%
Filter Cake	5.1	2.18	30%
Filtrate	10.9	5×10^{-16}	0.5%

The dewatered cake, containing 85 percent of the original solids, may be landfilled. The filtrate, when combined with the thickener overflow, would consist of 95 percent of the original water quantity and would have a suspended solids concentration of 4,000 mg/l.

A much clearer effluent could be obtained, of course, if all of the influent waste water were directly filtered. Such is the practice at Plant 006, which achieves an average phosphate removal efficiency of 95 percent.

Mechanical dewatering of lime precipitated phosphates by centrifugation was attempted, but it proved unsuccessful because the highly thixotropic cake plugged the solids-removal screw.

Because an excess of lime is used in the precipitation of the phosphates, the effluent from the ponds or from mechanical thickening and dewatering would have a high pH, typically 10 to 11. This effluent could be partially carbonated (with CO_2) to reduce the pH to 8.0 to 8.5 before discharge, with another filtration step to remove the calcium carbonate precipitate. Alternatively, it has been shown that subsequent activated sludge treatment of high pH waste water at municipal treatment plants lowers the pH due to biologically-released CO_2 from the oxidation of organic material.

Treatment Alternatives

There were two treatment alternatives considered for this subcategory. The first alternative is the treatment currently employed by 90 percent of the industry. This includes complete recycle of phossy water, evaporation of some process water, lime treatment, and sedimentation of the remaining water prior to discharge. The second alternative practiced by 10 percent of the industry, involved 100 percent recycle of all process water.

TREATMENT OF WASTE WATERS IN THE PHOSPHORUS CONSUMING SUBCATEGORY

Control and Treatment of Phossy Water at Phosphorus Producing Plants

Because of harmful effects of elemental phosphorus in small concentrations in waste water, and because complete removal of the phosphorus from the water is not practical, it is a universal practice at phosphorus-producing plants to reuse the phossy water after treatment (which is required to remove other constituents in the waste water which would otherwise build up to concentration).

Barber(5) discusses several methods which have been tried experimentally to remove elemental phosphorus from phossy water. Among these methods were chlorination, which was tried more than 20 years ago and which was discarded at that time because "accurate chlorinator control was found to be impractical." With the development of chlorine analyzer-controllers for municipal waste water treatment, however, it appears that chlorination deserves another trial. Air oxidation was attempted, but the reaction was far from complete, leaving 14 to 37 percent of the original colloidal phosphorus unoxidized. Filtration of the colloidal phosphorus was investigated but found impractical. As a result of these discouraging results, the industry has adopted the route of containment and re-use rather than treatment and discharge.

At the TVA Muscle Shoals plant, a commercial flocculant, at a concentration of 40 mg/l, is employed to settle both the phosphorus and the suspended solids. Using a clarifier, the system removes 92 to 93 percent of both the phosphorus and the suspended solids as phosphorus sludge underflow (which is only 2 percent of the waste water volume). The presence of suspended solids is necessary for efficient removal by this method.

The underflow from the clarifier may be treated as other phosphorus muds or sludges are treated. The sludge may be gravity thickened and/or dewatered by centrifugation or filtration. The sludge, thickened sludge, or sludge cake (with respectively lower moisture contents) may then be heat-dried in an inert atmosphere using the process byproduct carbon monoxide as fuel. Elemental phosphorus (nominally 40 to 65 percent of the "solids" in the sludge) are recovered. The remaining nonvolatile solids contain no elemental phosphorus and can be safely disposed of or recycled to the feed preparation section of the phosphorus manufacturing plant.

The clarifier overflow, containing only 7 or 8 percent of the original phosphorus and suspended solids, may then be recirculated to the phosphorus condenser sump and to other areas where water contacts phosphorus. However, because the phossy water accumulates dissolved salts (mainly fluorides and phosphates, see Table 7), about 6 percent of the clarified water must be bled off and discharged. In addition to suspended solids and dissolved solids, this bleed contains 120 mg/l of elemental phosphorus, equivalent to 0.4 kg/kkg, or 0.08 pound per ton, of product.

At Plant 181, a different approach is taken towards phossy water wastes. Very large lagoons not only reduce the concentration of suspended solids in the phossy water, but also serve to slowly oxidize much of the elemental phosphorus to phosphates. Subsequent lime treatment of the lagoon overflow (after combining with other waste water streams) precipitates not only the phosphates but also the fluorides in the water, thereby reducing the quantity of dissolved salts so that the water may be reused without a bleed. At this plant, the waste streams may be combined since all wastes are recycled without discharge.

A slightly different approach is taken at Plant 128. The phossy water is combined in a closed treatment and recycle system with calciner scrubber liquor. After settling of suspended solids and partial oxidation of phosphorus in a pond, lime treatment is used to precipitate dissolved phosphates and fluorides. Upon subsequent settling, the clarified (but still phossy) water is reused as calciner scrubbing water. Fresh make-up is used for the phosphorus condenser. The key to this scheme, which results in zero discharge of phossy water, is that the quantity of water vaporized in the calciner scrubber (in cooling the calciner tail gases) exceeds the quantity of phossy water in the raw waste load, so that fresh water may be continuously added to the loop without discharging any contaminated water.

Plant 159 achieves zero discharge of phossy water in a unique system. The completely segregated raw waste phossy water is sent to a clarifier in a manner similar to the TVA technique described above. The clarifier underflow of phosphorus sludge is treated in conventional ways, with complete return of the material to the process. The overflow from the clarifier is not recycled (as is the TVA practice, which requires a bleed discharge), but is sent to an evaporation pond.

In the approaches used by Plants 028 and 159, some or all of the phossy water is evaporated. This presents no hazard of elemental phosphorus, since it is very rapidly oxidized to phosphate as soon as the protective water is removed.

In summary, this study found three different ways that existing plants are achieving zero discharge of phossy water.

Treatment of Arsenic-Rich Residues

Arsenic-rich solid residues accumulate from the purification of phosphoric acid and of phosphorus pentasulfide. The common disposal method is burial in a controlled area, as practiced at Plants 075, 119, 147 and 192.

The arsenic-rich liquid residue from the PCl_3 distillation is more difficult to dispose of. At Plant 037 this residue is first treated with trichloroethylene, in which PCl_3 is miscible but $AsCl_3$ is not. The trichloroethylene is then water-washed to remove the arsenic-free PCl_3 and the trichloroethylene is reused. The $AsCl_3$-rich residue is then segregated and stored in drums for final disposal in an environmentally safe manner.

Treatment of Phosphoric Acid Wastes

The standard treatment of these wastes is by neutralization and/or precipitation with lime as discussed for the phosphorus production subcategory. The final product of neutralization, in an excess of lime and in a considerable excess of water, is formed:

$$6\ H_3PO_4 + 10\ Ca(OH)_2 \rightarrow 9\ CaO.3\ P_2O_5.Ca(OH)_2 + 18\ H_2O$$

Although this material is very insoluble, the reaction does not proceed to completion in practice unless a Ca/P mole ratio of at least 1.9 is reached. Moreover, the reactivity of the lime in precipitating the dissolved phosphate is strongly dependent on the lime source and the slaking conditions. It has been found that freshly slaked pebble quicklime can precipitate in excess of 97 percent of the phosphate, whereas commercial hydrated lime (calcium hydroxide) or freshly slaked ground quicklime only succeeded in a 73 to 80 percent precipitation efficiency under the same conditions.

A large body of literature has been developed in the lime treatment of domestic waste waters for phosphate removal. The study performed by Black & Veatch for EPA(31) summarizes the efforts that have been sufficiently demonstrated to be applied to current municipal waste water treatment projects. It is pointed out that the average concentration in domestic raw waste water is about 10 mg/l (expressed as elemental phosphorus). The domestic sources are about 1.6 kg (3.5 lbs) per capita per year, one-third of which are from human excretions and two-thirds from synthetic detergents.

The existing practice achieves better than 90 percent removal of the phosphates from domestic waste water, reducing the concentration (expressed as PO_4) from 30 mg/l to as low as 0.3 mg/l. At first glance, this seems to conflict with the fact that tricalcium phosphate (or hydroxylapatite) has a solubility of 25 mg/l (equivalent to 15 mg/l as PO_4). However, in a large excess of lime, the pH is sufficiently high (10 to 11) to reduce the solubility of this salt of a strong base and weak acid. The equilibrium

$$Ca^{+}_{3}(PO_4)_2(s) \longrightarrow 3Ca^{2} + PO_4^{-3} \xrightarrow{2H_2O} 3Ca^{+2} + 2OH^{-} + 2HPO_4^{-2}$$

is driven to the far left (reducing phosphate solubility) by the addition of excess lime. The solubility of tricalcium phosphate may be theoretically calculated as a function of pH (or of Ca:P ratio) using the ionization constants for H_3PO_4, $H_2PO_4^{-1}$, and HPO_4^{-2} in conjunction with a solubility product for tricalcium phosphate (which may be calculated from solubility data in pure water).

This phenomenon, substantiated by full-scale operating data as reported by Black & Veatch(31), is summarized below:

pH	Phosphate Concentration of Filtered Effluent, mg/l
9.0	5.7
9.5	1.4
10.0	0.6
10.5	0.3
11.0	0.2

The literature is replete with details of technology to achieve high removal efficiencies.(31-42) For example, thickened sludge recirculation to the neutralization tank has been found to seed the precipitation of calcium phosphate, resulting not only in better removal of dissolved phosphates but also in the growth of larger crystals for easier dewatering.

Although lime treatment of phosphates has been the predominant route, ferric chloride and alum have also been extensively used. Ferric salts are most effective in the 4 to 5 pH range and aluminum salts are most effective in the 5 to 6 pH range, as opposed to the 10 to 11 range for lime. The mole ratio of Fe/P or Al/P should be around 2.0, the same as the Ca/P ratio with lime treatment.

The use of lanthanum salts has recently been demonstrated to more effectively precipitate phosphates over a much wider pH range than calcium, ferric ion, or aluminum. The drawback is cost; the treatment system must recover and reuse the lanthanum.

Another process for phosphate removal is adsorption by activated alumina with subsequent stripping with caustic acid, and then regeneration of phosphate-free caustic by lime precipitation. Ion exchange has also been investigated.

One interesting process for phosphate removal is borrowed from a commercial process for HCl acidulation of phosphate rock. Phosphoric acid is recovered by solvent extraction, using C_4 and C_5 primary alcohols such as n-butanol and isoamyl alcohol. The chloride-free phosphoric acid is then extracted from the organic phase by water washing, the solvent is recycled, and the pure phosphoric acid may be concentrated by evaporation of water. This treatment method appears attractive for application to the food grade calcium phosphate waste streams. The suspended solids may be dissolved by HCl addition, and solvent extraction may be used to regenerate phosphoric acid for return to the process.

Treatment of Acidic Sulfite, Sulfate, and Phosphate Wastes

These acids are components of the waste streams from the phosphorus-consuming subcategory of the industry; and sulfuric acid is also a constituent of the wastes from the phosphorus production segment. The sulfurous and phosphorus acids may be partially oxidized prior to treatment to sulfuric and phosphoric acids.

The neutralization and precipitation of the slightly soluble calcium salts is exactly comparable to the treatment of acidic phosphate and fluoride wastes. The solubilities of calcium sulfite and of calcium phosphite are repressed by excess lime as in the previously discussed cases, but the solubility of calcium sulfate (a salt of a strong base and a strong acid) is not affected by pH.

Removal of Chlorides

Ion Exchange and Demineralization

Ion exchange and demineralizations are usually restricted in both practice and costs to total dissolved solids levels of 1000 to 4000 mg/l or less.

An ion exchange may be simply defined as an insoluble solid electrolyte which undergoes exchange reactions with the ions in solution. An exchanger is composed of three components: an inert matrix, a polar group carrying a charge, and an exchangeable ion carrying an opposite charge. The inert matrix is usually cross-linked polymeric resin containing the needed polar groups.

There are two types of ion exchangers: cation and anion. Cation exchangers contain a group such as sulfonic or carboxylic acid. These can react with salts to give products such as the following:

$$RSO_3H + NaCl \rightleftharpoons RSO_3Na + HCl$$
$$RCO_2H + NaCl \rightleftharpoons RCO_2Na + HCl$$

The above reactions are reversible and can be regenerated with acid.

Anion exchangers use basic group such as the amino family.

$$RNa_3OH + NaCl \rightleftharpoons RNa_3Cl + NaOH$$

This is also a reversible reaction and can be regenerated with alkalies. The combination of water treatment with both cation and anion exchangers removes the dissolved solids and is known as demineralization (or deionization). The quality of demineralized water is excellent. Table 16 gives the level of total dissolved solids that is achieved. Special ion exchange systems have been developed for treating high dissolved solids content (more than

TABLE 16. Water Quality Produced by Various Ion Exchange Systems

Exchanger Setup	Residual Silica, mg/l	Residual Electrolytes, mg/l	Specific Resistance ohm-cm @ 25 C
Strong acid cation + weak-base anion	No silica removal	3	500,000
Strong-acid cation + weak-base anion + strong-base anion	0.01-0.1	3	100,000
Strong-acid cation + weak-base anion + strong-acid cation + strong-base anion	0.01-0.1	0.15-1.5	1,000,000
Mixed bed (strong-acid cation + strong-base anion)	0.01-0.1	0.5	1-2,000,000
Mixed bed + first or second setup above	0.05	0.1	3-12,000,000
Similar setup as immediately above + continuous recirculation	0.01	0.5	18,000,000

1000 mg/liter total dissolved solids), minimizing regenerant chemicals costs.

Reverse Osmosis

The phenomenon of osmosis has its explanation in thermodynamic equilibrium and free energy concepts. Essentially, when a semi-permeable membrane separates a pure liquid and solution of dissolved material in the same liquid, there is a net migration of the pure liquid to the solution, driven by the free energy difference between the two sides of the membrane. Equilibrium is reached only when the liquids on each side of the membrane are of the same composition, or sufficient additional pressure is applied on the solution side of the membrane to counterbalance the osmotic driving force. Application of additional pressure on the solution side reverses the direction of osmotic flow through the membrane and results in concentration of the solution and migration of additional pure liquid to the pure liquid side. This is reverse osmosis. It may be looked at as pressure filtration through a molecular pore-sized filter.

The small pore size of the reverse osmosis membrane is both its strength and its weakness. Its strength comes from the molecular separations that it can achieve. Its weakness comes from the criticalness it has to blinding, plugging, and chemical attack. Acidity, suspended solids, precipitations, coatings, dirt, organics and other substances can make it inoperative. Membrane life is critical and unknown in many mediums.

With these restrictions there is little wonder that its industrial applications are few. Fortunately, the phosphorus chemicals industry water purification needs are similar to those of the areas where reverse osmosis has been shown to be applicable -- treatment of brackish water and low (500 mg/l to 20,000 mg/l) dissolved solids removal. Organics are usually absent, suspended solids are low and can be made low rather easily, acidity is easily adjusted, and the dissolved solids are similar to those in brackish water -- sodium chlorides, sulfates and their calcium counterparts.

Evaporation Ponds

Plant 159 utilizes an evaporation pond for disposal of phossy water from phosphorus manufacturing. They may also be reasonably used for other waste water disposal where the waste water quantities are not overwhelming.

The size of an evaporation pond depends on the climatic differential between evaporation and rainfall:

Evaporation-Rainfall Differential	Pond Area
0.6 m/yr (2 ft/yr)	0.060 ha/cu m/day (560 acres/MGD)
1.2 m/yr (4 ft/yr)	0.030 ha/cu m/day (280 acres/MGD)
1.8 m/yr (6 ft/yr)	0.020 ha/cu m/day (190 acres/MGD)

Evaporation ponds may be either unlined or lined, and should be diked. Use is often made of natural pits, valleys or ponds.

Conventional evaporation ponds are not, of course, among the useful treatments in areas where the rainfall exceeds the evaporation. However, surface aerators (commonly used for aerated lagoons in secondary treatment of organic wastes) can significantly increase the evaporation from a pond by increasing the water/air surface area.

Single-Effect and Multiple-Effect Evaporators

For the treatment of small waste streams, single-effect evaporators are characterized by low equipment costs and by inherent reliability, at the expense of high steam requirements. Conventional multiple-effect evaporators, with 2 to 6 effects, have somewhat higher capital costs, but require much less steam.

Evaporation is a technology, of course, that is aptly demonstrated throughout the chemicals process industry (although not extensively for the sole purpose of waste treatment), and as such meets the requirements of being currently available.

Refrigerated Condensers for PCl_3 and $POCl_3$

In the standard processes for manufacturing PCl_3 and $POCl_3$, the present industry practice is to use water cooled condensers to reflux the reaction vapors and to collect the product. Because the vapor pressure of PCl_3 is significantly high (boiling point 76°C (169°F)) at normal condensing temperatures, the raw waste load in the tail-gas water scrubbers contains rather large quantities of the hydrolysis products of PCl_3. The use of refrigerated condensers in place of the water-cooled condensers, or alternately, the use of cold traps downstream of the water-cooled condensers, would drastically reduce the amount of PCl_3 in the tail gas which subsequently becomes acid aqueous wastes:

Temperature, °C	Temperature, °F	PCl_3 Vapor Pressure, mm Hg(27)
-40	-40	3
-20	- 4	13
0	32	38
+20	68	99
+40	104	235

It is apparent that a condensing temperature below -20°C (-4°F) would lower the PCl_3 vapor pressure by an order of magnitude over normal condensing temperatures and would virtually double the temperature driving force for heat transfer.

Refrigerated condensers are in current use (for $POCl_3$ manufacture using air oxidation) at Plant 037.

Inert-Atmosphere Casting of P_2S_5

The present industry practice is to cast molten P_2S_5 product into shipping containers or into conical forms. When molten P_2S_5 is exposed to the atmosphere, it spontaneously ignites, forming P_2O_5 and SO_2 which are subsequently water-scrubbed.

There are various state-of-the-art techniques available for casting either in an inert atmosphere or in vacuum, to eliminate this source of raw aqueous waste.

Treatment Alternatives

The treatment alternatives considered for the manufacture of phosphoric acid are additional treatment (the only discharges are from leaks and spills) and no discharge of any process waste water pollutants to navigable waters. The latter alternative involves tightened housekeeping and maintenance construction of dikes and dams around pumps, valves, and tanks; construction of sumps and sump pumps; lime treatment of leaks and spills; and landfill of the sludge. This is currently practiced by 10 percent of the industry.

There were two treatment alternatives considered for the manufacture of phosphorus pentoxide: no additional treatment and no process waste water discharge.

Three treatment alternatives were considered for the manufacture of phosphorus pentasulfide. The first involves no additional treatment. The second includes reduction of the volume of waste water discharge by the recycle of scrubber water. The third alternative includes no waste water discharge, lime treatment, settling tanks, recycle of tank overflow back to the process, and landfill of sludge.

Several treatment alternatives were considered for the manufacture of phosphorus trichloride and phosphorus oxychloride. The first alternative is no treatment. The second involves reduction of waste water volume by recycle of scrubber water. The third alternative includes lime treatment, settling tanks, and landfilling of sludge. The fourth alternative involves no discharge of process waste water pollutants to navigable waters.

TREATMENT OF WASTE WATERS IN THE PHOSPHATE SUBCATEGORY

Treatment of Specific Wastes

Sodium Tripolyphosphate Manufacture

As stated in Section V, two notable plants (042 and 119) achieve no discharge of process waste waters. Airborne solids collected in dust collectors from the spray dryer gaseous effluent stream are added to the product. Scrubber water is used to form a slurry with caustic in the initial neutralization step.

The manufacture of sodium tripolyphosphate is therefore a water consuming process, requiring no waste water treatment.

Calcium Phosphates Manufacture

The amount of airborne solid wastes removed by wet scrubbers can be minimized by preceding wet scrubbers with dry dust collection equipment. Treatment of phosphoric acid, suspended solids, and sludges resulting from wet scrubbing has been previously described for the phosphorus production subcategory.

Wet phosphoric acid is frequently used for animal feed grade phosphates. Fluosilicic, hydrofluoric and silicic acid wastes will subsequently result from acid defluorination. Treatment of these parameters has also been discussed previously for the phosphorus production subcategory.

Treatment Alternatives

The only treatment alternative considered for the manufacture of sodium tripolyphosphate is no discharge of process waste water pollutants.

Two treatment alternatives were considered for the manufacture of feed grade dicalcium phosphate. The first, employed by at least 50 percent of the industry, involves in-process controls for phosphate and lime dusts and phosphoric acid mists. The second alternative includes the above plus lime treatment settling, recycle of clarified water to the acid scrubbers and landfill of the sludge.

Three treatment alternatives were considered for the manufacture food grade dicalcium phosphate. No treatment is the first alternative. In the second alternative baghouses replace wet scrubbers with product recovery. Approximately 30 percent of the industry is practicing this technology. In the third alternative waste water is treated with lime, filtered, and recycled in the process. The filter cake is landfilled. Approximately 10 percent of the industry is achieving no discharge of process water pollutants by this technology.

SECTION VIII

COSTS, ENERGY AND NON-WATER QUALITY ASPECTS

INTRODUCTION

The control and treatment technologies applicable to the raw wastes of the phosphate manufacturing industry were discussed in Section VII of this report. In this Section, each of these technologies is reviewed from the following standpoints:

* The cost of applying the technology.
* The energy demands of the technology.
* The impact of the technology on air quality, solid waste management, noise and radiation.
* The recovery and subsequent use of process materials from raw waste streams, as a result of applying the technology.

A representative, hypothetical plant for each chemical produced in the industry is synthesized. Cost-effectiveness data for the plant for the various treatment alternatives (see table 17) appear as table 18. The cost is in terms of both investment cost and equivalent annual cost; and the effectiveness, in terms of pollutant quantities, is compared to the raw waste load. The discussion of costs and benefits in this Section, however, is formulated to be more generally useful in evaluating the economics for any particular plant within the industry. Costs for a specific plant may be significantly influenced by the following factors which cannot all be incorporated into a single hypothetical plant:

> The degree of freedom, which the personnel of each plant must retain, to choose among the alternative control and treatment technologies presented in Section VII, to choose from technologies not presented in this report, and to choose any combination or permutation of these technologies.
>
> The cost tradeoffs, which are unique for each plant, between in-process controls and end-of-process treatments, with material recovery being an important parameter.
>
> The real raw waste load for each plant, which may be appreciably different (in either direction) from the standard raw waste loads as presented in Section V. In particular, much greater plant-to-plant variability was observed with respect to production-normalized raw waste water quantities than with respect to production-ion-normalized raw quantities of polluting constituents.

TABLE 17

TREATMENT ALTERNATIVES

Subcategory	Chemical	Alternative	Description
Phosphorus Producing	P_4 (Fe_2P)	A	Existing control complete recycle of phossy water. Evaporation of some other process water. Lime treatment and sedimentation of remaining process water prior to discharge.
		B	Piping, pumping, and controls for 100% recycle of process wastewaters.
Phosphorus Consuming	H_3PO_4	A	No treatment. (Only wastewaters orginate from leaks, spills, etc.)
		B	Tighten housekeeping and maintenance. Dike and dam around pumps, valves,, tanks, etc. Provide sumps and sump pumps. Treat with lime and landfill the sludge.
	P_2O_5	A	No treatment.
		B	Lime treatment, settling tank, recycle of tank overflow back to process, and landfill sludge.
	P_2S_5	A	No treatment.
		B	Recycle scrubber water.
		C	Lime treatment, settling tank, recycle tank overflow back to process, landfill sludge + B.
	PCl_3	A	No treatment.
		B	Recycle scrubber water.
		C	Lime treatment, settling tank and landfill sludge + B.
		D	Evaporation + B + C.
	$POCl_3$	A	No treatment.
		B	Recycle scrubber water.
		C	Lime treatment, settling tank, and landfill sludge + B.
		D	Evaporation + B + C.
Phosphate Producing	$Na_5P_3O_{10}$	A	Dry dust collection already in existance at exemplary plant. May be economically justified on the basis of product recovery.
	$CaHPO_4$	A	In-process controls for phosphate and lime dusts and for phosphoric acid mists, including dry dust collection and scrubber water recycle to process.
		B	Lime treatment, settling pond, recycle of clarified water to acid scrubbers, and landfill sludge. + A.
	$CaHPO_4$ Feed grade	A	Replace wet scrubbers with baghouses.
		B	Lime treatment, filtration of slurry, recycle of filtrate, and landfill of filter cake + A.

TABLE 18

TREATMENT ALTERNATIVES
COST - EFFLUENT QUALITY COMPARISON

Chemical	Treatment Alternative	% Industry Using Alternative	Investment $1,000	Annual Operating Costs $1,000	Cost Per Units $/Kkg	Wastewater l/Kkg	TSS Kg/Kkg	TDS Kg/Kkg	Acidity Kg/Kkg	F Kg/Kkg	SO_4 Kg/Kkg	PO4 Kg/KKg	H_3PO_4 & H_3PO_3 Kg/Kkg	H_3PO_4 Kg/Kkg	H_2SO_3 Kg/Kkg	HCl Kg/kkg	HF, H_2SiF_6 H_2SiO_3 Kg/Kkg	pH
Phosphorus	**Subcategory**																	
P_4	Raw Waste	-	-	-	-	426,000	42	-	54	54	111	25						
	A	90	-	-	-	104,000	0.5	4	1.5	0.1	2	0.2						
	B	10	500	228.2	5.07	0	0	0	0	0	0	0						
Phosphorus	**Consuming Subcategory**																	
H_3PO_4	Raw Waste (A)	90	-	-	-	8												
	B	10	95	42.9	0.67	0												
P_2O_5	Raw Waste (A)	100	-	-	-	500							0.2					
	B	0	20	9.1	1.54	0							0					
P_2S_5	Raw Waste (A)	100	-	-	-	30,000							0.5	1				
	B	0	12.5	5.6	0.44	3,000							0.5	1				
	C	0	49.5	22.8	1.87	0							0	0				
PCl_3	Raw Waste (A)	100	-	-	-	5,000	-	-					2.5			3		2
	B	0	4.2	1.8	.17	500	-	-					2.5			3		1.5
	C	0	16.5	8.8	.77	420	0.7	5					0			0		6-10.5
	D	0	20.5	18.3	1.54	0	0	0					0			0		-
$POCl_3$	Raw Waste (A)	100	-	-	-	2,500	-	-					0.5			2		2
	B	0	2.2	1.0	.16	250	-	-					0.5			2		1.5
	C	0	14.2	6.9	.94	210	0.2	3.5					0			0		6-1-.5
	D	0	15.9	10.1	1.38	0	0	0					0			0		-
Phosphate	**Subcategory**																	
$Na_5P_3O_{10}$	Raw Waste	-	-	-	-	0												
	A	100	*	*	*	0												
$CaHPO_4$ (Feed Grade)	Raw Waste	-	-	-	-	6,700	22					4					12	
	A	50	*	*	*	6,300	22										12	
	B	50	186	91.6	1.54	0	0										0	
$CaHPO_4$ (Food Grade)	Raw Waste	60	-	-	-	4,200	100								30			
	A	30	*	*	*	2,100	50								15			
	B	10	200	135.0	2.30	1,800	0.06								0.03			6-10

---

* Use of dry dust collection and product recovery will cover cost of this alternative, hence, no costs were listed.

There is a wide variation in the existing application of effluent control technology. Some plants have more equipment to install than others in order to meet the effluent limitations guidelines. In addition physical characteristics of each particular plant will affect treatment costs such as:

- Plant age, size, and degree of automation.
- Plant layout (i.e., can in-process controls be physically installed between existing units?).
- Plant distances and topography (i.e., what are the installation and operating costs of recycle technologies?).
- Climatic factors (temperature and evaporation/rainfall).
- Esthetic factors (i.e., is a settling pond locally acceptable?).
- Land availability (primarily a factor in applying settling pond and evaporation pond technologies).

The degree to which a plant is integrated with other production departments would significantly affect the cost of applying control and treatment technologies. Can waste materials from one department be used in an adjoining department (i.e., mutual neutralization of acid and alkaline wastes)? Can common treatment facilities be built (tradeoff between economies of scale vs. reversing the principle of segregation of wastes)? Are the waste water sewers from adjoining departments readily separable? The feasibility and attractiveness of joint municipal/industrial waste water treatment, which is a highly local evaluation to be made. Increasingly, more examples of such dual treatment are being reported.

The local solid waste management situation. The sludges from applying waste water treatment technologies may be landfilled at highly different costs, depending on the local availability of disposal sites and the distances involved.

In appreciation of all of the above factors, the discussion of costs in this section is formulated to be generally useful in evaluating the economics for any particular plant within the industry.

Definition of Representative Plants

The sizes of the representative plants were chosen so that their capacities were approximately the averages of the data presented in table 2. Although in many cases (especially in the phosphorus consuming segment of the industry) more than one product is made at a given location, each product was addressed separately in this supplement. Cost savings due to combined treatment facilities are a distinct probability. The effect in practice would be to achieve the benefits at costs lower than those presented in this analysis.

The particular assumptions in choosing representative plants were:

1. Phosphorus Manufacture--The representative plant has already no discharge of phossy water (as much of the industry has). It has, in addition, achieved a level of effluent reduction commensurate with that of plant 028 (see Tables 13 and 14), but still discharges 25,000 gallons of treated process water per ton into a receiving stream. Technology "A" of Table 17, therefore, represents effluent reduction, with respect to the raw waste load, already achieved by the representative plant, with no additional costs required. The effluent from technology "A" is suitable for process re-use, and technology "B" is the implementation of this recycle. For the representative plant, it was assumed that the return water system traversed 1,000 yards back to the head end of the plant and had a difference in elevation of 60 feet. It was also assumed that the representative plant had no severe freezing problems.

2. Phosphoric Acid Manufacture--The representative plant had no process water discharge (including phossy water), but had not yet performed a systematic and thorough program for minimizing, collecting, and treating minor phosphoric acid leaks and spills.

3. Manufacture of P_2O_5, P_2S_5, PCl_3, and $POCl_3$--The representative plants for these chemicals had not yet instituted any control or treatment of acid waste waters, but have already achieved zero discharge of phossy water. As a conservative approach for PCl_3 and $POCl_3$ manufacture, it was assumed that solar evaporation for technology "C" in Table 17 was not feasible for climatic reasons so that mechanical evaporators were necessary. It was also assumed that refrigerated condensers proved less economical than larger evaporators.

The representative plants for P_2O_5, P_2S_5, PCl_3, and $POCl_3$ are assumed not to have sufficient land for settling ponds, so that mechanically raked clarifiers are used.

4. Sodium Tripolyphosphate Manufacture--The representative plant has either of two situations: (a) Dry dust collection with return of solids and wet scrubber liquors to the process has already been installed, resulting in zero discharge of process waste waters. (b) The above controls have not been installed, but can be economically justified on the basis of product recovery.

For either of these two situations (which cover much of the industry), no additional costs (attributable to effluent reduction benefits) are required.

5. Feed Grade Dicalcium Phosphate Manufacture--For control of phosphate and lime dusts and phosphoric acid mists, the representative plant has no additional required costs (attributable to effluent reduction benefits), for the same reasons as listed above for sodium tripolyphosphate manufacture.

It is assumed, however, that the representative plant uses wet-process phosphoric acid and that it performs defluorination of all acid used (in practice, a good fraction of received acid may already be defluorinated). It is further assumed that the representative plants have sufficient land area for on-site settling ponds.

6. Food-Grade Calcium Phosphate Manufacture--The representative plant is assumed to have wet scrubbers for dust-laden vent streams. Technology A of table 17 shows the replacement of wet scrubbers with baghouses, but the cost is justified by product recovery. It is assumed that at this representative plant the elimination of wet scrubbers reduces the waste load by 50 percent.

Current Selling Prices

Table 3 shows the current list prices of the chemicals within this industry. These data are useful as a yardstick for measuring the economic impact of achieving pollution control.

Capital Cost Basis

For these analyses, the capital investment costs have been adjusted to 1971 dollars using the Chemical Engineering Plant Cost Index (1957-59 = 100; 1971 = 132.2). The capital recovery segment of the annual costs is based on a 5-year amortization schedule, consistent with IRS regulations concerning pollution-abatement equipment and facilities, and on an 8 percent interest rate. The resulting annual capital recovery factor (principal and interest) is 0.25046.

"Taxes and Insurance" annual cost is estimated at 5 percent of the investment cost. "Operating and Maintenance" annual cost includes labor, supervision, lab support, etc., and is estimated at 15 percent of the investment cost, exclusive of chemicals, energy and power costs (which are calculated directly for each appropriate case). Chemical costs are included in "Operating and Maintenance," but power is listed separately. The cost of lime for neutralization has been assumed at $20 per ton, and the cost of steam for evaporation has been assumed as $0.70 per thousand pounds (or $0.70 per million BTU).

In-Process Controls

The cost of these controls are perhaps the most difficult to generalize, since they are almost wholly dependent on the existing equipment configuration in any particular plant.

Segregation of Waste Streams

First, a plant must be surveyed to pinpoint the sources of both process water and non-contact cooling water. At one plant, there were numerous points where process water entered a common sewer, but there were relatively few cooling water sources. It was much more economical to divert the cooling water to a new and separate collection system than to adopt the reverse strategy. The project costs for such a retrofit would be highly labor intensive, especially since the construction must proceed without unduly disrupting production schedules. Other than capital recovery and associated annual costs, the annual costs would consist of a small maintenance cost and no costs for operating labor, materials or power.

There would be no effect of this project on energy demands, since plant sewers are normally gravity flow. There would be no adverse non-water quality impacts of this project.

Recycle of Scrubber Water

The capital costs would be to provide a surge tank, a recycle pump, and associated piping. The surge tank need not be large; a 15-minute residence time should suffice. The power costs and energy use of the pump would not greatly exceed the corresponding values presently utilized to provide fresh scrubber water at comparable flow rates. In any event they are small since scrubber flow rates are small.

Dry Dust Collection

Based on data furnished by the personnel of Plant 007, the capital cost of high-temperature baghouses for this 91 kkg/day (100 tons/day) plant was $350,000. The annual operating and maintenance costs, other than capital recovery, taxes and insurance, is estimated at 6 percent of the capital cost. A credit to the annual cost is the value of recovered material; the quantity might be estimated as 2 to 5 percent of the production rate, since baghouses recover virtually all dusts. The power requirements for the fans and shakers are small, and are usually comparable to the pump power requirements for the liquid scrubbing systems they replace. Since the recovered dusts are almost always utilized in the process, there is no adverse impact on solid waste management.

Refrigerated Condensers

The condensers are standard items, and in practice the existing condensers may be used. The refrigeration supply is standard equipment, and rather expensive in terms of capital costs. An added cost would be the insulation of existing coolant lines and of the condenser. The power requirement for the refrigeration compressor could be moderately high. There would not be impact on non-water quality aspects.

Inert-Atmosphere Casting for P_2S_5

This is a relatively expensive control technique, requiring major revisions not only of the casting equipment but also of the basic casting procedures. There would be some small power requirements, either for inert-gas blowers or for vacuum pumps. The annual cost of the inert gas (assuming it is not recycled) must be estimated.

Housekeeping and Containment

Like the previously-discussed project of water segregation, housekeeping and containment capital costs are labor-intensive and depend to a very large extent on the existing plant configuration. A point of reference might be taken from the experience of one 360 kkg/day (400 tons/day) plant which expended $160,000 for isolation and containment (trenches, sewers, pipelines, sumps, catch basins, tanks, pumps, dikes and curbs). The need to attend to many small sources of leaks and spills reduces the economies of scale. The power requirements are minimal, limited to small sump pumps. No adverse non-water quality impacts arise from this control technique.

TREATMENT OF SPECIFIC WASTE CONSTITUENTS

Neutralization of Acidic Waste Waters and Precipitation of Calcium Salts

A general cost factor for neutralization is 1.3 to 5.3 cents per cu m (5 to 20 cents/1,000 gallons). However, the cost for lime is directly dependent not on the waste water quantity but on the total acidity. The data of table 8, with a lime cost of \$22/kkg (\$20/ton), can be used to calculate this cost.

Neutralization tanks are usually small, with residence time varying from 30 seconds to 30 minutes. The installed cost of these tanks may be approximated by:

$$\text{Capital Cost} = \$15{,}000\ {\frac{\text{GPD}}{10{,}000}}^{0.2}$$

(Note: 1/day = 3.785 x GPD)

The power requirements for mixing are rather nominal. Assuming subsequent sedimentation or other dewatering operations, the neutralization step alone does not have any adverse non-water quality impacts.

Treatment of Arsenic-Rich Residues

The cost of this solvent is rather nominal because the quantities of waste involved are only a very small fraction of the production volume, and because the solvent (trichloroethylene) is reused, despite the high unit cost which is more than 10 cents/cu m (40 cents/1,000 gal). There is virtually no power requirement. There is, however, a very substantial impact on solid waste management, since the residues are extremely objectionable and must be disposed of in special ways. The quantity involved is 0.05 kg of $AsCl_3$ per kkg of product PCl_3 (0.1 lb/ton).

Control and Treatment of Phossy Water

Control and treatment of phossy water is a universal practice at phosphorus-producing plants. Although several different methods were observed, every plant prevents the discharge of virtually all elemental phosphorus. This technology is therefore so widely applied that costs need not be estimated; the price has already been paid. Similarly, a discussion of energy and of non-water quality aspects would be academic.

Removal of Suspended Solids

Settling Ponds

Using a detention time of 7 days and a depth of 3 m (10 ft), the calculated overflow rate is 0.42 cu m/day/m^2 (10 gpd/ft^2). This is equivalent to 4,200 cu m/day/hectare (435,600 gpd/acre).

The capital costs for small unlined ponds, with areas from 0.4 to 2 hectares (1 to 5 acres) can be estimated as:

$$\text{Capital Cost} = \$50{,}000 \times \text{Acres} - \$8{,}000 \times (\text{Acres})^{2}$$

(Note: Hectares = 0.405 x Acres)

Because diking is a large portion of pond costs, and because the dike length increases much more slowly than pond area, larger ponds are considerably cheaper per unit area. For large unlined ponds of 40 to 1,000 hectares (100 to 2,400 acres), the capital cost is $2,500 to $12,500 per hectare ($1,000 to $5,000 per acre).

For lined ponds, the additional installed capital cost for a 30-mil PVC liner is $21,500 per hectare ($8,700 per acre). By using the above overflow rate and the above pond costs per unit area, a pond cost based on waste water flow may be calculated.

Settling ponds utilize no energy. The solids do, however, collect on the bottom and must either be periodically removed (creating a solid waste disposal problem), or the filled pond may be abandoned and replaced with a new one (creating a land use problem).

Mechanically-Raked Clarifiers and Thickeners

A general cost for gravity thickening is 0 to 2.6 cents per cubic meter (0 to 5 cents per 1,000 gallons).

The installed cost of mechanically-raked clarifiers and thickeners with capacities of 38 to 38,000 cu m/day (0.01 to 10 MGD) can be estimated as:

$$\text{Capital Cost} = \$95{,}000\ (\text{MGD})^{0.4}$$

(Note: Cu m/day = 3,785 x MGD)

Where polymeric flocculants are used, the additional cost amounts to $4 per kg of flocculant ($1.80/lb). The dosage rate is nominally 0.05 kg/kkg of dry sludge solids (0.1 lb/ton).

The power requirements are nominal, since the rake has a very long period of revolution. Additional nominal power requirements arise from sludge pumping and clarifier overflow pumping.

This treatment has (by definition) a solid waste impact, since its function is the removal of suspended solids. The sludge from thickeners may be 85 to 92 percent moisture. If the quantities are small, this sludge may be directly transported to landfills. Alternately, it may be dewatered on sand drying beds or mechanically (filters or centrifuges) to 60-70 percent moisture before landfilling. The quantity to be landfilled is therefore a very strong function of the degree of dewatering after thickening.

Vacuum Filtration and Centrifugation

The costs of these two mechanical dewatering techniques are competitive. A general cost for either is 0 to 2.6 cents per cubic meter (0 to 5 cents per 1,000 gallons).

The installed capital costs for either vacuum filters or centrifuges are as follows:

Capacity, MGD	cu m/Day	Installed Cost
0.01	38	$25,000
0.1	378	25,000
1	3785	200,000
10	37850	750,000

Polymeric flocculants are often used to condition the sludge before dewatering. These costs were discussed in the previous paragraph.

The power requirements for vacuum filtration are moderate; they include the sludge pump, the flocculant pump, the rotating conditioning tank, the vacuum filter drum drive, the sludge agitator below the filter drum, the vacuum pump, the filtrate pump and the cake conveyor belt. Centrifuges have much larger power requirements, since the sludge must be accelerated to hundreds or several thousands of G's. At high speeds, the windage losses (air friction) of centrifuges are considerable. Large centrifuges may require 40 to 75 Kw (50 to 100 HP) of power. Auxiliary power is also required for sludge pumping, flocculant pumping, centrate pumping, the cake scraper, and the cake conveyor belt.

Vacuum filters and centrifuges have a beneficial impact on solid waste management. Rather than landfilling 12 percent sludge, these devices drastically reduce the solid waste quantity by producing a 30 to 40 per-cent cake.

Centrifuges have a moderately adverse impact with regard to noise pollution, since they run with a characteristic high speed whine that is annoying to the human ear. Vacuum filtration is also noisy.

Landfilling of Solid Wastes

The disposal costs for solid wastes are highly dependent on the hauling distance. The landfill operations alone may cost $6 or more per kkg (or per ton) for small operations and $2 to 4 per kkg (or per ton) for larger operations.

Several pertinent papers have recently been published on the subject of solid waste management in the chemical industry.(63,64)

Solid waste hauling and the material handling operations at landfills are energy consuming operations. Landfilling of containerized soluble solids in plastic drums or sealed envelopes is practicable but expensive. Blow-molded plastic drums, made from scrap plastic (which is currently one of the major problems in solid waste disposal), could be produced for $11-$22/kkg ($10-$20/ton) capacity at 227 kg (500 pounds) solids/drum and a rough estimate of $2.50-$5.00 cost/drum. A more economical method, particularly for large volumes, would be sealed plastic envelopes, 750 microns (30 mils) thick.

At $1.10/kg (50¢/lb) of film, low density polyethylene costs about 10¢ per 0.0929 square meter (1 square foot). Using the film as trench liner in a 1.8 meters (6-foot) deep trench, 1.8 meters (6 feet) wide, the perimeter (allowing for overlap) would be approximately 7.5 meters (25 feet). At a density of 1.6 grams/cc (100 pounds/cubic foot) for the solid, costs of plastic sheet per metric ton would be $2.00 ($1.75/ton). With sealing, the plastic envelope cost would be approximately $2.20/kkg ($2/ton). With additional landfill costs of $2.20/kkg ($2/ton), the total landfill disposal costs would be about $4.40/kkg ($4/ton).

The above figures for solubles disposal using plastic containers, bags, or envelopes are only rough estimates. Also, the technology would not be suitable for harmful solids or in situations where leaching contamination is critical.

Removal of Chlorides

Demineralization and Reverse Osmosis

These treatments are costly, over 10 cents per cubic meter (40 cents per 1,000 gallons).

The installed capital costs can be calculated from:

a. Demineralization, Cap. Cost = $280,000 (MGD)0.75
b. Reverse Osmosis, Cap. Cost = $480,000 (MGD)0.75

Hence, the capital costs for reverse osmosis are nearly double those for demineralization.

The operating costs (not including capital recovery costs) are:

a. Demineralization, 20 cents/1,000 gal @ 1,000 mg/l TDS
40 cents/1,000 gal @ 2,000 mg/l TDS
b. Reverse Osmosis, 38 cents/1,000 gal @ 0.01 MGD
20 cents/1,000 gal @ 0.1 MGD
14 cents/1,000 gal @ 1 MGD

Neither demineralization nor reverse osmosis requires a great deal of power, and neither has significant non-water quality impact.

Solar Evaporation Ponds

The installed costs of solar evaporation ponds (on the basis of pond area) are essentially the same as the costs for settling ponds presented earlier. The pond area depends in this case on the climatic differential between evaporation and rainfall:

Evaporation-Rainfall Differential	Pond Area
0.6 m/yr (2 ft/yr)	0.060 ha/cu m/day (560 acres/MGD)
1.2 m/yr (4 ft/yr)	0.030 ha/cu m/day (280 acres/MGD)
1.8 m/yr (6 ft/yr)	0.020 ha/cu m/day (190 acres/MGD)

The power requirements and non-water quality aspects of solar evaporation ponds are the same as for settling ponds. Since the residue in this case is soluble, extra disposal precautions must be taken to prevent leaching into groundwaters.

Single-Effect and Multiple-Effect Evaporators

The installed capital and operating costs for single-effect evaporators and for a 6-effect evaporator (all stainless-steel construction) are as follows:

	Installed Capital Costs		O & M Costs, $/1,000 gal	
Capacity, GPD	1 Effect	6 Effects	1 Effect	6 Effects
10,000	8,000		5.64	
50,000	28,000		5.51	
100,000	45,000	177,000	5.45	1.30
250,000	80,000	373,000	5.39	1.22
500,000	146,000	665,000	5.36	1.18
1,000,000	267,000	1,225,000	5.33	1.14

(Note: Liters = 3.785 x Gallons)

The energy requirements for single-effect evaporators are 555 kg-cal per kilogram of water evaporated (1,000 Btu/lb), while the 6-effect evaporator requires 100 kg-cal per kilogram of water evaporated (180 Btu/lb). The non-water quality aspects are the same as for solar evaporation ponds.

NON-WATER QUALITY IMPACT

Air Pollution

The proposed guidelines are not expected to increase air emissions. In fact, the cited technologies should decrease air emissions in some cases where dry air pollution equipment is suggested to precede wet scrubbers. Volatilization of hazardous substances, such as fluorine, from ponds is not expected to present a problem since addition of lime will precipitate most fluorides.

Solid Waste

Solid waste disposal will be the chief non-water quality area impacted by the proposed guidelines. Neutralization of acidic waste streams with lime or limestone will increase the amounts of sludge, especially when soluble phosphates and sulfates are precipitated. Installation of dry air pollution control equipment will reduce the water content of wasted solids. In addition, return of collected solids to the process may be feasible. As stated in section VII, arsenic rich solid residues accumulate from the purification of phosphoric acid and of phosphorus pentasulfide. Burial in a controlled area is the standard disposal method. Special disposal methods as mentioned previously in this section may be necessary to prevent leachate from reaching surface or ground waters. Solid waste quantities and constituents are listed in Tables 9 and 10.

Energy Requirements

The energy requirements for the proposed treatment technologies are listed in table 19. For the best practicable control technology currently available the added energy requirements are insignificant when compared to the process energy requirements. Except for the production of phosphorus, energy does not significantly enter into the product cost. For best available technology economically available, the additional energy requirements for PCl_3 and $POCl_3$ are substantial. This is due to the assumption that solar evaporation ponds may not be possible in a given locale and evaporators may be necessary.

Ground Water

Since settling and evaporation ponds are extensively used for waste water treatment in the phosphate industry, it is highly recommended that all such ponds be sealed or lined so as to prevent any leakage of contaminated process waters to ground waters.

Noise

No overall adverse affect on the level of noise is expected, although individual equipment may have excessive noise levels; e.g., pumps and centrifuges.

TABLE 19

ENERGY REQUIREMENTS FOR RECOMMENDED GUIDELINES

Chemical	Process Energy Requirement KWH/Kkg	Treatment Energy Requirement KWH/Kkg	Percentage Energy Increase
P_4	15,400	7.06	0.05
H_3PO_4	48	0.000025	0.01
P_2O_5	94	0.0126	0.01
P_2S_5	9	0.75	8.3
PCl_3 (BPCTCA)	27	0.13	0.48
PCl_3 (BATEA	27	293	1000
$POCl_3$ (BPCTCA)	28	0.063	0.22
$POCl_3$ (BATEA)	28	146	520
$Na_5P_3O_{10}$	43	0	0
Calcium Phosphates animal feed grade	-	0.16	-
Calcium Phosphates food grade	-	0.053	-

BPCTCA - best practicable control technology currently available

BATEA - best available technology economically achievable

SECTION IX

EFFLUENT REDUCTION ATTAINABLE THROUGH THE APPLICATION OF THE BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE

INTRODUCTION

The effluent limitations which must be achieved by July 1, 1977, are based on the degree of effluent reduction attainable through the application of the best practicable control technology currently available. For the phosphate industry, this level of technology is based on the best existing performance by notable plants of various sizes, ages and chemical processes within each of the industry's categories. In some cases where no truly notable plants were surveyed, this level of technology is based on state-of-the-art unit operations commonly employed in the chemical industry.

Best practicable control technology currently available emphasizes treatment facilities at the end of a manufacturing process but also includes the control technology within the process itself. Examples of in-process control techniques which are used within the industry are:

* manufacturing process controls
* recycle and alternative uses of water
* recovery and/or re-use of waste water constituents
* dry collection of airborne solids instead of (or before) wet scrubbing.

Consideration was also given to:

a. The total cost of application of technology in relation to the effluent reduction benefits to be achieved from that application;

b. The size and age of equipment and facilities involved;

c. The process employed;

d. The engineering aspects of the application of various types of control techniques;

e. Process changes; and

f. Non-water quality environmental impact (including energy requirements).

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PROCESS WASTE WATER GUIDELINES

Process water is defined as any water coming into contact with raw materials, intermediates, products, by-products, or gas or liquid that has accumulated such constituents. All values of guidelines and limitations for total dissolved solids (TDS), total suspended solids (TSS), metals and harmful pollutants and and other parameters are expressed as consecutive 30-day averages in units of pounds of parameter per ton and kilograms of parameter per metric ton of product produced except where expressed as a concentration.

On the basis of the information contained in Sections III through VIII of this report, the following determinations were made on the degree of effluent reduction attainable with the application of the best practicable control technology currently available in the phosphate manufacturing industry.

The Phosphorus Production Subcategory

Phossy Water

Because of the extremely harmful nature of elemental phosphorus, it is standard practice within the industry to maintain tight control over the discharge of phossy water, as discussed in Section VII.

It is apparent from the discussion in section VII that existing practicable technology can eliminate the requirements for any discharge at the TVA plant. Lime treatment of the blowdown followed by sedimentation of the precipitated phosphates and fluorides would remove the materials necessitating a blowdown, so that this treated blowdown could be recombined with the remainder of the clarified phossy water for return to the process.

There are three examples of plants which have achieved zero discharge of phossy water: Plants 159, 028, and 181.

Hence, three plants have recognized the undesirability of elemental phosphorus in any discharge and have also recognized that no practicable treatment system can remove a sufficient amount of elemental phosphorus to permit effluent discharge of phossy water wastes. They have all solved this dilemma by evaporating sufficient phossy water rather than by discharge. One plant uses an evaporation pond, while two others exploit other process heat loads for in-process water evaporation.

In view of this clear-cut demonstration within the industry, it is recommended that the best practicable control technology currently available for phossy water wastes be no discharge of pollutants to navigable waters.

Process Waters Other Than Phossy Water

The standard techniques for treating the waste waters from calciner scrubbers and from slag quenching are lime treatment and settling ponds, which perform the following functions:

- Neutralization of acid waste waters;
- Sedimentation of much of the original suspended solids in the waste waters (silica, iron oxide, and others);
- Precipitation and sedimentation of much of the phosphates, fluorides and sulfates which were dissolved in the original waste waters;
- Dissipation of the process heat to the atmosphere during the extended residence in the settling ponds;
- Reduction in the waste water quantity as a result of net evaporation during the extended residence in the settling ponds;and
- Where phossy water is combined with these other process waters, some oxidation of the elemental phosphorus to phosphates is accomplished.

At Plant 181, the lime-treated water from all sources is clarified in settling ponds, and the clarified water is held in re-use water supply ponds. There is total recycle of all water at this plant, with zero discharge. Because phosphates and fluorides are removed by lime treatment and sedimentation, there is no requirement to bleed off water for the control of dissolved solids.

Under conditions of very abnormally high rainfall which would exceed the capacity of the pond system, the only overflow would be from the final re-use water supply ponds, thereby minimizing the quantities of pollutants even occasionally discharged. The recirculating water system runs at a water deficit, due to evaporation in the process and to net evaporation in the pond system. Hence, fresh make-up water is supplied, and can be controlled to compensate for temporary swings in the pond evaporation/rainfall balance.

The TVA plant at Muscle Shoals, Alabama granulates the slag by quenching with a high-velocity jet of water which is recirculated from a sump in the slag pit. In this TVA operation, the cooling water and the scrubber liquors are used for make-up in slag quenching. The granulated slag effectively neutralizes these waters and also acts to filter out the scrubbed solids, which become part of the slag pile to be sold. Nearly all of the soluble phosphate and 95 percent of the fluoride is removed by the slag, and the fluoride concentration is reduced to 30 mg/l. Hence, TVA utilizes slag treatment instead of lime treatment because the slag is finely divided. Sufficient waste water treatment is obtained by TVA to enable the plant to completely reuse this water without any discharge.

Two other phosphorus plants which utilize lime treatment and sedimentation for process water treatment are Plants 028 and 159. Tables 14 and 15 list (respectively) the effluent concentrations and quantities discharged from these plants, neither of which recycles treated waste water. There are three significant differences between these two plants:

* Plant 028 discharges into the same waterway as the plant intake so that its discharge responsibility is the net increase in constituent quantities. Plant 159 intakes ground water and discharges into surface water so that its responsibility is the gross amount of constituent quantities.

* It is apparent from the "Intake" columns of Tables 14 and 15 that the intake of Plant 159 contains much more dissolved solids (and specifically F, PO_4 and SO_4) than the intake of Plant 028.

* The waste water quantity percent of production for Plant 028 is three times that of Plant 159.

The above three differences are interrelated and affect the quantities of fluoride, phosphate and sulfate discharged by Plant 159 because the effluent concentrations are of the same magnitude as the solubilities of the corresponding calcium salts. Hence, the effluent quantities are significantly influenced by factors other than the treatment of the process waters.

The effectiveness of control and treatment techniques used by the four phosphorus plants cited are summarized in Table 13. Plants 028 and 159 achieve very high (97% to 99+%) control and treatment efficiencies and correspondingly low quantities (although not absolutely zero) of discharged constituents.

In areas of the country where very severe and extended cold weather prevails, total recycle of process water becomes difficult for two reasons:

1. The return water piping and pumping must be protected against freezing. However, technology such as buried water mains and enclosed, heated pumping stations has been amply demonstrated in the chemical industry and in water supply operations.

2. The settling ponds may freeze. In a total recycle system, this circumstance would prevent the required water from being supplied back to the process. If auxiliary fresh water supply were provided to uncouple the process from frequent climatic perturbations, the pond system would have to consist of sufficient holding capacity to prevent temporary overflow and would have to contain sufficient evaporative capacity to prevent long-term accumulation of water.

Recommended Effluent Limitations Guidelines Based Upon Best Practicable Control Technology Currently Available

In view of the existence of three plants (028, 159 and 181) which have already achieved zero discharge of elemental phosphorus, in view of the existence of one plant (181) which has already achieved zero discharge of all process waters, and in view of two plants (028 and 159) that are achieving exemplary performance, it is recommended that the best practicable control technology currently available for a period of 30 consecutive days be:

Total suspended solids	0.5 kg/kkg (1.0 lb/ton)
Total phosphorus	0.15 kg/kkg (0.3 lb/ton)
Fluoride	0.05 kg/kkg (0.10 lb/ton)
Elemental phosphorus	No detectable quantity
pH	Within the range 6.0 - 9.0

Waste Water from Ore Washing or Beneficiation

The best practicable control technology currently available recommended in the previous paragraphs does not include wastes from the beneficiation or washing of phosphate rock. This beneficiation is commonly but not exclusively conducted at a separate off-site location. The huge raw waste load from beneficiation, 7.5 kkg of gangue per kkg of phosphorus eventually produced, warrants a separate study and separate effluent limitations guidelines.

The Phosphorus Consuming Subcategory

Phossy Water

Gross discharges of phossy water are presently avoided by pumping displaced phossy water from the plant's phosphorus storage tank back into the emptying rail car which brought the phosphorus, and by transporting this displaced phossy water to the phosphorus producing plant for treatment and/or re-use. Such is the practice at Plants 037 and 192.

Smaller quantities of phossy water discharge may also be eliminated through the use of standard engineering techniques. The phosphorus storage tank level control system may be altered to provide an auxiliary water overflow tank with return of the water to the main tank. The avoidance of elemental phosphorus in plant sewer lines can be implemented with more stringent process and operator controls and procedures and by providing traps downstream of reaction vessels.

In view of the harmful qualities of elemental phosphorus and in view of the available choices from state-of-the-art control techniques, the recommended best practicable control technology currently available for phossy water is no discharge of pollutants.

Phosphoric Acid Manufacture

Exemplary Plant 075 operates without the discharge of any process water. There is no fundamental or practical reason why process water should be discharged at all from any dry-process phosphoric acid plant. Minor leaks and spills may be minimized, collected and treated using control techniques generally available and demonstrated in the industry.

The recommended effluent limitations guideline of no discharge of process waste water pollutants applies generally, and with special emphasis, to elemental phosphorus (i.e., phossy water) and to arsenic residues from the purification of phosphoric acid.

Phosphorus Pentoxide Manufacture

The single raw waste constituent is phosphoric acid from water tail-gas seals. Application of two standard techniques would enable total recycle of this waste water:

1. Reduction in waste water quantites by using dilute caustic or lime slurry as tail gas liquor instead of pure water, increasing the absorptive capacity for P_2O_5.

2. Lime treatment and sedimentation to neutralize and to remove the phosphate, permitting total recycle.

In view of the straightforward application of these two techniques, the recommended best practicable control technology currently available for phosphorus pentoxide manufacture is no discharge of process waste water pollutants to navigable waters. Since total recycle is practicable technology, this recommended guideline is not affected by modest inaccuracies in the standard raw waste as estimated in Section V.

Phosphorus Pentasulfide Manufacture

The sole source of process waste water is the scrubber liquor for fumes from casting liquid P_2S_5. One control technique would be the use of inert-atmosphere casting or vacuum casting to completely eliminate the need for scrubbing. As an alternate to this approach, the application of three standard techniques would permit total recycle of scrubber water:

1. Use of dilute caustic or lime slurry instead of pure water would reduce the waste water quantities by increasing the adsorptive capacity for P_2O_5 and SO_2.
2. Partial recycle of scrubber liquor from a sump would reduce the waste water quantity by decoupling the buildup of absorbed acids from the mass-transfer requirements for high scrubber flow rates.
3. Lime treatment and sedimentation to neutralize and to remove phosphate, sulfite and sulfate would permit total recycle.

In view of these different practicable alternatives, the recommended best practicable control technology currently available for phosphorus pentasulfide manufacture is no discharge of process waste water pollutants to navigable waters. Since total recycle is practicable technology, this recommended effluent limitations guideline is not affected by modest inaccuracies in the standard raw waste load as estimated in Section V.

This effluent limitations guideline also applies to any arsenic-rich residues from the purification of P_2S_5; these solid residues may be disposed of by burial as in Plants 147 and 192.

Phosphorus Trichloride Manufacture

The acid wastes from phosphorus trichloride manufacture arise from the hydrolysis of PCl_3 in scrubber water from the reactor/still from product storage tanks, from product transferring operations, and from container cleaning. The scrubber water may be collected in a sump and recycled to decrease the wasted quantity of scrubber water (while still maintaining sufficient scrubber flow rates for effective mass transfer) and to increase the concentration of waste constituents.

Lime treatment of the wasted water would neutralize the acids and would precipitate the phosphite and phosphate wastes as calcium salts. Subsequent sedimentation in a mechanically-raked clarifier, with the use of a polymeric flocculant, could effectively remove 85 percent of the suspended solids as a sludge. This sludge may then be hauled as a slurry for direct landfill or may be dewatered in sand drying beds or mechanically before landfilling. The clarified water may then be discharged, with the following recommended best practicable control technology currently available:

Total Phosphorus	0.8 kg/kkg (1.6 lb/ton)
Total Suspended Solids,	0.7 kg/kkg (1.4 lb/ton)
Arsenic	0.00005 kg/kkg (0.0001 lb/ton)
pH	6.0 to 9.0

based on the raw waste load as determined in Section V:

HCl	3 kg/kkg (6 lb/ton)
$H_3PO_3 + H_3PO_4$	2.5 kg/kkg (5 lb/ton)

The soluble $CaCl_2$ resulting from lime-neutralization of HCl is 4.5 kg/kkg (9 lb/ton); allowing for some small amount of unprecipitated phosphite and phosphate brings the total dissolved solids to 5 kg/kkg (10 lb/ton). The quantity of precipitated $2\ CaHPO_3.3H_2O$, $Ca_3(PO_4)_2$, or $9\ CaO.3P_2O_5.Ca(OH)_2$ is dependent on the relative quantities of these compounds, but is no more than 4.5 kg/kkg (9 lb/ton). With a sedimentation efficiency of 85 percent, the total suspended solids in the effluent should be no more than 0.7 kg/kkg (1.4 lb/ton).

In the case of PCl_3 manufacture, the soluble chlorides are not removed by the applicable "best practicable control technology currently available," so that the recommended best practicable control technology currently available is not zero discharge. In treating the raw wastes, the total quantity of constituents is not reduced: 5.5 kg/kkg (11 lb/ton) in the raw waste vs. 5.7 kg/kkg (11.4 lb/ton) in the treated effluent. However, the treatment does remove the acidity, substituting for it residual alkalinity.

Zero discharge of arsenic-rich reactor/still residues is recommended, since trichloroethylene treatment (as described in Section VII) may be applied.

Phosphorus Oxychloride Manufacture

The types of raw wastes, the types of applicable control and treatment technologies, and the reason for the best practicable control technology currently available not being zero discharge, are all identically parallel for $POCl_3$ manufacture as they are for PCl_3 manufacture. The difference is one of magnitude. For $POCl_3$ manufacture, the raw waste load as determined in Section V is:

HCl	2 kg/kkg (4 lb/ton)
$H_2PO_3 + H_3PO_4$	0.5 kg/kkg (1 lb/ton)

Using the same rationale as for PCl_3 manufacture, the recommended best practicable control technology currently available effluent limitations guideline are:

Total Phosphorus	0.17 kg/kkg (0.34 lb/ton)
Total Suspended Solids,	0.15 kg/kkg (0.3 lb/ton)
pH	6.0 to 9.0

The Phosphate Subcategory

Sodium Tripolyphosphate Manufacture

Exemplary Plant 042 has no process wastes. The dust collected from the spray-dryer gaseous effluent stream is added to the spray-dryer solid product stream. The water used for subsequent scrubbing of this gas stream from the spray dryer is then recycled to the mix area and is used as process water in the neutralization step. The cooling air used for the product tempering is vented into the spray-dryer vent line upstream of the scrubbing operation.

This plant is an excellent example where a combination of in-process controls such as dry dust collection, water re-use, and return to the process of airborne solids have been utilized to totally avoid any aqueous wastes. Plants 006 and 119 also have no discharge of process waters.

In view of this demonstration, and in view of the general applicability of such techniques throughout the industry, the recommended best practicable control technology currently available is no discharge of process waste water pollutants to navigable waters.

Animal-Feed Grade Calcium Phosphates

Exemplary Plant 182 has no process wastes. Three separate water cycles are used, and there is no effluent from any of them. The acid defluorination scrubber water is neutralized with lime, the solids are settled by ponding, and the pond effluent is reused as scrubber water. The scrubber water for collection of airborne solids from the reactor and dryer is recirculated with a bleed-off directly into the reactor as process water. Cooling water is recycled through a cooling tower, with the blowdown used as make-up in the solids scrubbing system instead of being wasted. Softened well water is used for cooling water make-up.

This plant is an excellent example where a combination of in-process controls (dry dust collection, recycle of scrubber water to minimize waste water quantities, return of process waste streams to the process, and a systems approach towards water use whereby a blowdown stream from one water cycle becomes a make-up stream for another) in combination with a standard lime-treatment, sedimentation and total recycle scrubber water system results in the discharge of no aqueous wastes.

In view of this demonstration, and in view of the general applicability of such techniques throughout the industry, the recommended best practicable control technology currently available is no discharge of process waste water pollutants to navigable waters.

Food-Grade Calcium Phosphates

The raw aqueous wastes from the manufacture of food grade calcium phosphates are from two primary and approximately equal sources: the centrate or filtrate from dewatering of the dicalcium phosphate slurry, and the effluent from wet scrubbers which collect airborne solids from product drying operations. Both of these sources contain suspended, finely divided calcium phosphate solids and phosphoric acid from acid units and from excess acid in the reaction liquid. The total raw waste load (from Section V) is:

Process Water Wasted	4,200 l/kkg (1,000 gal/ton)
Total Suspended Solids (2.4%)	100 kg/kkg (200 lb/ton)
Phosphoric Acid (0.7%)	30 kg/kkg (60 lb/ton)

The first type of currently available control technology that may be applied is the substitution of dry dust bag collectors for wet scrubbers, as has been done at Plants 003, 042, 119, and 182. The fact that a multi-product plant must provide a separate baghouse for each product does not deny the current availability of this technology, but rather increases the cost of such an installation. However, Plant 003, which is a multiple-product, food grade, calcium phosphates plant, has justified the installation of separate baghouses on the sole basis of profitability from product recovery.

The elimination of wet scrubbing systems would halve the aqueous waste load so that it would then consist of 2,100 l/kkg (500 gal/ton), containing 2.4 percent of suspended solids amounting to 50 kg/kkg (100 lb/ton) and containing 0.7 percent of phosphoric acid amounting to 15 kg/kkg (30 lb/ton).

Lime treatment, clarification and sedimentation (with the aid of polymeric flocculant) may then be used to precipitate the phosphate and remove suspended solids to 25 mg/l. The clarifier underflow will remove the bulk of the suspended solids. Dewatering of these solids may be required to make them suitable for landfill. The practice at Plant 006 after lime treatment for neutralization and precipitation of phosphate wastes is vacuum filtration of the slurry from the clarifier underflow. The water lost with the solids reduces the effluent flow to 1800 l/kkg (430 gal/ton) containing:

Suspended Solids	0.06 kg/kkg (0.12 lb/ton)
Total Phosphorus	0.03 kg/kkg (0.06 lb/ton)

SUMMARY OF PROPOSED BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE

No Discharge of Process Waste Water Pollutants

The proposed best practicable control technology currently available for process waste water is no discharge of pollutants for the manufacture of the following chemicals:

- Phosphorus Consuming Subcategory
  - Phosphoric Acid (Dry Process)
  - Phosphorus Pentoxide
  - Phosphorus Pentasulfide
- Phosphate Subcategory
  - Sodium Tripolyphosphate
  - Calcium Phosphates (Animal-Feed Grade)

Permitted Discharge

The proposed best practicable control technology currently available for process water for the manufacture of phosphorus (and ferrophosphorus), PCl_3, $POCl_3$ and food grade calcium phosphate require that the average of daily values for 30 consecutive days shall not exceed:

	Phosphorus and Ferrophosphorus	Phosphorus Trichloride	Phosphorus Oxychloride	Food Grade Calcium Phosphate
Suspended Solids kg/kkg	0.5	0.7	0.15	0.06
Total Phosphorus kg/kkg	0.15	0.8	0.17	0.03
Fluoride kg/kkg	0.05			
Arsenic kg/kkg		0.00005		
pH	6.0-9.0	6.0-9.0	6.0-9.0	6.0-9.0

The above guidelines apply to maximum averages of daily values for any period of 30 consecutive days.

The pH range is to be maintained at all times.

The permitted maximum concentration for any one day period for suspended and dissolved solids is twice that of the consecutive 30 day average value.

SECTION X

EFFLUENT REDUCTION ATTAINABLE THROUGH THE APPLICATION OF THE BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE

INTRODUCTION

The effluent limitations which must be achieved by July 1, 1983, are based on the degree of effluent reduction attainable through the application of the best available technology economically achievable. For the phosphate manufacturing industry, this level of technology was based on the very best control and treatment technology employed by a specific point source within the industrial category or subcategory, or where it is readily transferable from one industry process to another. Best available technology economically achievable places equal emphasis on in-process controls as well as on control or treatment techniques employed at the end of a production process.

Those plant processes and control technologies which at the pilot plant, semi-works, or other level have demonstrated both technological performances and economic viability at a level sufficient to reasonably justify investing in such facilities were also considered in assessing the best available technology economically achievable. This technology is the highest degree of control technology that has been achieved or has been demonstrated to be capable of being designed for plant scale operation up to and including "no discharge" of pollutants. Although economic factors are considered in this development, the costs for this level of control are intended to be for the top of the line of current technology subject to limitations imposed by economic and engineering feasibility. However, best available technology economically achievable may be characterized by some technical risk with respect to performance and with respect to certainty of costs. Therefore, this technology may necessitate some industrially sponsored development work before its application.

The following factors were taken into consideration in determining the best available technology economically achievable:

a. The age of equipment and facilities involved;

b. The process employed;

c. The engineering aspects of the application of various types of control techniques;

d. Process changes;

e. Cost of achieving the effluent reduction resulting from application of best available technology economically achievable;and

f. Non-water quality environmental impact (including energy requirements).

PROCESS WATER GUIDELINES

Process water is defined as any water coming into contact with raw materials, intermediates, products, by-products, or gas or liquid that has accumulated such constituents.

On the basis of the information contained in Sections III through IX of this report, the following determinations were made on the degree of effluent reduction attainable with the application of the best available control technology economically achievable in the various categories of the phosphate manufacturing industry.

All Chemicals Except Phosphorus, Phosphorus Trichloride, Phosphorus Oxychloride and Food Grade Calcium Phosphate

The recommended best available technology economically achievable for process water are the same as the best practicable control technology currently available effluent limitations guidelines, i.e., no discharge of process waste water pollutants to navigable water for the manufacture of the following chemicals:

- Phosphorus-Consuming Subcategory
    - Phosphoric Acid (Dry Process)
    - Phosphorus Pentoxide
    - Phosphorus Pentasulfide
- Phosphate Subcategory
    - Sodium Tripolyphosphate
    - Calcium Phosphates (Animal Feed Grade)

The Phosphorus Production Subcategory

At Plant 181, the lime-treated water from all sources is clarified in settling ponds, and the clarified water is held in re-use water supply ponds. There is total recycle of all water at this plant, with zero discharge. Because phosphates and fluorides are removed by lime treatment and sedimentation, there is no requirement to bleed off water for the control of dissolved solids.

Under conditions of very abnormally high rainfall which would exceed the capacity of the pond system, the only overflow would be from the final re-use water supply ponds, thereby minimizing the quantitites of pollutants even occasionally discharged. The recirculating water system runs at a water deficit, due to evaporation in the process and to net evaporation in the pond system. Hence, fresh make-up water is supplied, and can be controlled to compensate for temporary swings in the pond evaporation/rainfall balance.

It is therefore recommended that the best available control technology economically achievable for phosphorous production be no discharge of process waste water pollutants to navigable waters.

Manufacture of Phosphorus Trichloride and Phosphorus Oxychloride

In-Process Controls

The largest contribution to the raw waste load from these processes is from the escape of PCl_3 vapor from the reactor/stills. The methods for drastically reducing this contribution are clear cut: the substitution of refrigerated condensers for water-cooled condensers or the addition of refrigerated condensers downstream of water-cooled condensers. Refrigerated condensers are already in use at Plant 037 in the manufacture of $POCl_3$ by the air-oxidation process.

As an added step, a demister can be added downstream of the refrigerated condenser to prevent condensed but dispersed PCl_3 from escaping to the scrubber. One concept for this demister is a short section of column packed with metal packing (for good heat transfer) within the refrigerated condenser.

As a corollary to this principle, other sources of PCl_3 and $POCl_3$ vapors could be controlled by refrigerated condensers or cold traps. The storage tank vent and vents for the transfer of liquid products are included in this concept. Alternatively, the liquid products could be maintained at low temperatures by refrigerating coils in the storage tanks so that vapors from storage and transfer would be minimized.

In view of the order-of-magnitude or greater reduction in the vapor pressure of these products resulting from readily available refrigeration levels, plus the effect on PCl_3 condensation from doubling (or more) the temperature driving force for heat transfer, a reasonable expectation is that the PCl_3 vapor (and mist) losses could be cut to 10 percent of the present values.

The acid wastes from washing tank cars and tank trucks, and from washing used $POCl_3$ filter elements are very small at present, amounting to 0.014 kg/kkg (0.028 lb/ton) of HCl and 0.003 kg/kkg (0.007 lb/ton) of total phosphates (see table 8). These are very small fractions of the total raw waste load discussed in section V. The wastes from washing returnable nickel drums, however, is estimated to be much larger. Should this raw waste indeed prove significant, the returnable container use could be abandoned in favor of non-returnable, epoxy-lined drums (as is the partial practice at Plant 147 for PCl_3).

Another minor source of waste water is the generation of HCl (not PCl_3) from the reactor/stills, resulting from small quantities of stray moisture in the vessels. The HCl is driven off as a non-condensible while the corresponding H_3PO_3 and H_3PO_4 is retained as reactor residue.

All in all, the above outlined in-process control techniques could drastically reduce the raw waste load to perhaps 10 percent of the original value, so that the estimated raw waste quantities would then become (for either PCl_3 or $POCl_3$ manufacture):

HCl	0.3 kg/kkg (0.6 lb/ton)
H_3PO_3 + H_3PO_4	0.25 kg/kkg (0.5 lb/ton)

As important as the reduction in the waste water constituent quantities would be a corresponding reduction in the quantity of waste water generated. Tail-gas scrubbers should be very much smaller and should require much lower water flow rates.

As an added step, the scrubber water could be recycled from a sump, thereby decoupling the waste water quantity (blowdown from the sump) from the mass-transfer requirements for scrubbing. Furthermore, water use could be cascaded in the plant; for example, the waste water from tank car washing could be used as make-up in the tail-gas scrubber system.

End-of-Process Treatment

At the new low levels of waste water flow rates and constituent quantities, simple lime neutralization of moderate pH (without sedimentation) would result in the following waste water characteristics:

Waste water Quantity	500 l/kkg (120 gal/ton)
Total Dissolved Solids	0.5 kg/kkg (1.0 lb/ton)
Total Suspended Solids	0.35 kg/kkg (0.7 lb/ton)
pH	6-9

Further lime neutralization and removal of suspended solids would not appreciably reduce the quantity of total dissolved solids, and would trade off reduction in total suspended solids for higher pH levels.

At this point, the waste water quantity would be extremely low, and a practicable final step would be evaporation to dryness. An idea of the costs of evaporation can be obtained by assuming a plant manufacturing 59 kkg/day (65 tons/day) of total PCl_3 and $POCl_3$. The waste water quantity would be 30,000 liters/day (7,800 gal/day). Using the data of Section VIII for single-effect evaporation,

Capital Cost = $6,700
Annual Costs: Capital Recovery = $ 1,600
Taxes & Insurance = 300
Operation & Maintenance = 14,700
(including energy) $16,600
Unit Cost = $0.85/kkg ($0.77/ton)

This unit cost is only 0.3 percent of the current selling price, $295/kkg ($268/ton).

It is entirely possible that a rigorous economic evaluation might result in a decision to dispose of the original raw waste load by evaporation, rather than to bear the expense of the in-process controls discussed above which minimize (but do not eliminate) the waste. The waste water quantity to be evaporated would be the original quantity, 5,000 l/kkg (1,200 gal/ton), or 300,000 liters/day (78,000 gal/ton); and the costs would be:

Capital Cost = $38,400
Annual Costs: Capital Recovery = 8,900
Taxes & Insurance = 1,900
Operation & Maintenance = 147,000
(including energy)
Unit Cost = $8.10/kkg ($7.35/ton)

The most conservative approach, i.e., to evaporate all of the waste water without any in-process control to reduce its quantity, would cost 2.8 percent of the current selling price. The fundamental reason is that despite the high unit cost of evaporating water, the waste water quantities for PCl_3 and $POCl_3$ are very small. The conclusion is reached that the application of this available technology is economically achievable.

The final step of total evaporation would bring the PCl_3 and $POCl_3$ manufacturing processes into line with the rest of the phosphate industry by achieving the national goal of eliminating the discharge of all pollutants.

It is therefore recommended that the best control technology economically achievable for PCl_3 and $POCl_3$ manufacture be no discharge of process waste water pollutants to navigable waters.

Food Grade Calcium Phosphate Manufacture

After elimination of wet scrubbers as described in Chapter IX standard lime treatment and sedimentation may be used to neutralize these remaining wastes, to precipitate the phosphate, and to remove a nominal 85 percent of the suspended solids (with the possible aid of a polymeric flocculant). At a pH of 10.5, the remaining concentration of dissolved solids would be approximately 0.3 mg/l. The quantity of waste water would be approximately 85 percent of concentration of dissolved solids with the remainder landfilled with the underflow from the clarifier as wet sludge. The clarified overflow would than consist of 1,800 l/kkg (430 gal/ton) containing:

Dissolved Solids	0.0005 kg/kkg (0.001 lb/ton)
Suspended Solids	11 kg/kkg (22 lb/ton)

The demonstrated practice at Plant 006, after lime treatment for neutralization and for precipitation of phosphate wastes, is vacuum filtration of all of the slurry from the clarifier underflow.

Vacuum filtration (possibly after conditioning with a polymeric flocculant) can reduce the suspended solids content of the waste water from phosphates to the level of 0.5 mg/l. Based on these data and on the level of dissolved phosphates of 0.3 mg/l, the discharge would contain on the basis of the total process water wasted, 4,200 l/kkg (1,000 gal/ton):

Total Dissolved Solids	0.0015 kg/kkg (0.003 lb/ton)
Total Suspended Solids	0.0025 kg/kkg (0.005 lb/ton)

With the achievement of these extremely low levels of TDS and TSS, or even with considerable relaxation of these levels, the treated-waste water from the manufacture of food grade calcium phosphate is expected to meet the U.S. Food and Drug Administration criteria for process water and this treated water can then be recycled back into the process. No product purity restrictions exist any longer which had previously necessitated discharge. In fact, once the commitment to total recycle is made, the lime treatment step may be bypassed since the ionic species from the dissolved solids and the phosphoric acid are precisely those desired in the reaction vessel. However, the problem of waste segregation is sufficiently great that for reasons of product purity existing plants may not be able to make the necessary changes by 1977.

It is therefore recommended that the best available control technology economically achievable for food grade calcium phosphate manufacture be no discharge of process waste water pollutants to navigable waters.

SECTION XI

NEW SOURCE PERFORMANCE STANDARDS AND PRETREATMENT RECOMMENDATIONS

INTRODUCTION

This level of technology is to be achieved by new sources. The term "new source" is defined in the Act to mean "any source, the construction of which is commenced after publication of proposed regulations prescribing a standard of performance." New source performance standards are to be evaluated by adding to the consideration underlying the identification of best available technology economically achievable a determination of what higher levels of pollution control are available through the use of improved production processes and/or treatment techniques. Thus, in addition to considering the best in-plant and end-of-process control technology identified in best available technology economically achievable, new source performance standards are to be based on an analysis of how the level of effluent may be reduced by changing the production process itself. Alternative processes, operating methods and other alternatives were to be considered. However, the end result of the analysis identifies effluent standards which would reflect levels of control achievable through the use of improved production processes (as well as control technology), rather than prescribing a particular type of process or technology which must be employed. A further determination which was to be made for new source performance standards is whether a standard permitting no discharge of pollutants is practicable.

The following factors were considered with respect to production processes which were analyzed in assessing new source performance standards:

a. The type of process employed and process changes;

b. Operating methods;

c. Batch as opposed to continuous operations;

d. Use of alternative raw materials and mixes of raw materials;

e. Use of dry rather than wet processes (including substitution of recoverable solvents for water); and

f. Recovery of pollutants as by-products.

PROCESS WATER GUIDELINES

On the basis of the information contained in Sections III through X of this report the following determinations were made on the degree of effluent reduction attainable with the application of new source standards for the various categories of the phosphate manufacturing industry.

Since the best practicable control technology currently available effluent limitations guidelines for all of the chemicals considered in this study of the phosphate category were no discharge of process waste water pollutants to navigable waters, the recommended new source performance standards are identical to the best available technology economically achievable.

PRETREATMENT RECOMMENDATIONS

In addition to the recommendation of new source performance standards and related effluent limitations covering discharges directly into waterways, the constituents of the effluent discharge from a plant which would interfere with, pass through, or otherwise be incompatible with a well designed and operated publicly owned activated sludge or trickling filter waste water treatment plant were identified. A determination was made of whether the introduction of such pollutants into the treatment plant should be completely prohibited.

Waste Water Flow Rate

A determination must be made on an individual basis about the impact of a plant's discharge on the total hydraulic capacity of both the municipal collection system and the municipal waste water treatment plant. At an extreme, hydraulic overloading will result in overflows or by-passes as the capacities of pumping stations (both in the collection system and the raw waste water pumping stations at the treatment plant) are exceeded. It must be remembered that an overflow of combined industrial/municipal waste water has the same adverse environmental effect as an overflow of raw domestic sewage. At a minimum, hydraulic overloading would result in reduced efficiency of the treatment plant because:

* Primary and secondary clarifiers would be operating at excessive overflow rates;
* Secondary treatment units (activated sludge or trickling filters) would be operating at a food deficiency since the waste water from the phosphorus chemicals industry would provide no organic material;
* Trickling filters would become flooded (and so anaerobic);
* Grit chambers would have a high linear velocity resulting in the carry-over of grit and the subsequent adverse effects on equipment;
* The capacity of air blowers for activated sludge secondary treatment may be exceeded, resulting in reduced

levels of dissolved oxygen;

- The capacity of chlorinators may be exceeded, resulting in insufficient disinfection; and
- The critical operating parameters of the activated sludge unit may be compromised.

The domestic waste water flow rate follows a well-known diurnal cycle; if the industrial contribution could be staggered to provide flow equalization, the impact of the added flow rate could be minimized. Conversely, sporadic slug discharges could make periodic overloading more probable.

Suspended Inorganic Solids

High concentrations of suspended inorganic solids might overload the primary sludge collectors, the primary sludge pumps, the sludge thickener, the sludge dewatering operation, and the sludge disposal system. In addition, since these solids provide no organic food for secondary treatment organisms, they would reduce the active biological-solids fraction (i.e., reduce the mixed liquor volatile suspended solids), thereby reducing the efficiency of secondary treatment.

Acidity

While moderate alkalinity may be tolerated since carbon dioxide produced in secondary treatment by the microbial oxidation of organic material will provide neutralization, free mineral acidity normally cannot be tolerated by the organisms in the secondary treatment biomass. The proteins in these organisms are precipitated and coagulated at pH 4 to 5.

Another strong reason for avoiding acidic contributions to publicly-owned treatment plants is that acidic wastes would drastically promote corrosion of equipment.

It is recommended that the allowable pH range be set at 6 to 10.5.

Dissolved Inorganic Solids

Dissolved inorganic solids would pass through a secondary waste water treatment plant without being removed. Hence, reliance on publicly owned treatment plants would be no treatment at all with respect to dissolved solids, and it would be equivalent to direct discharge.

The pretreatment standards for dissolved inorganic solids should be the same as the applicable or proposed effluent limitations guidelines.

Heavy Metals or Harmful Materials

Metals or harmful materials would at best, pass through a publicly owned treatment plant, and at worst, adversely affect the microorganisms in secondary treatment. Elemental phosphorus (as phossy water) and enriched arsenic compounds are substances that may be discharged into municipal sewer systems from this industry. Special attention is brought to pretreat wastes for removal of these materials.

It is recommended that the pretreatment standards be no discharge of metals or harmful materials.

Dissolved Phosphates

While dissolved phosphates would generally pass through secondary treatment plants with the waste water treatment plant effluent, they would affect the sludge operations. Gravity-thickened sludge (6 to 12 percent solids) is normally conditioned with lime, ferric chloride, or alum before dewatering operations, although polymeric flocculants are also widely used. The phosphates would be precipitated as the calcium, ferric, or aluminum phosphate and would thus render the conditioning step ineffective by partially or totally removing the active cation from solution.

A similar situation exists in tertiary treatment, in the phosphate removal step using lime, ferric chloride, or alum. In this case, the chemical requirements would be increased and the sludge handling capacity of the treatment plant could be overloaded. While these pretreatment standards apply only to secondary plants, precautions should be taken to avoid adverse effects when tertiary treatment might be added in future years.

Summary of Recommended Pretreatment

Due to the nature of the process waste waters of the phsophorus producing and the phosphorus consuming subcategories it is recommended that these wastes not be discharged into publicly owned treatment works. These waste waters are considered to be incompatible with such works principally because of harmful constituents such as elemental phosphorus and the possible presence of arsenic, cadmium, uranium and like metals also present in the phsohate ore.

The principal contaminant from the phosphate subcategory is phosphate, which is incompatible with secondary treatment plants. However, these wastes are considered to be compatible with tertiary treatment plants designed, constructed and operated to remove dissolved phosphates.

SECTION XII

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Mr. Ernst Hall, Effluent Guidelines Division
Mr. Walter J. Hunt, Effluent Guidelines Division
Mr. Elwood Martin, Effluent Guidelines Division
Dr. Chester Rhines, Effluent Guidelines Division
Mr. Michael Kosakowski, Effluent Guidelines Division
Mr. Harry Trask, Office of Solid Waste Management Programs
Mr. John Savage, Office of Planning and Evaluation
Mr. Taylor Miller, Office of General Counsel
Mr. Srini Vasan, Region V
Dr. Edmond Lomasney, Region VI
Ms. Begina Carroll, Office of Technical Services
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SECTION XIII

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SECTION XIV

GLOSSARY

All underlined numbers within a chemical formula represent normally subscripted numbers. Physical limitations of the printing device make this system necessary. For Example, H_2O represents water.

Barn

A room-like condensation chamber for anhydrous phosphorus pentoxide.

Burden

The combined rock, coke and silica feed to a phosphorus electric furnace.

Calcination

Heating of a solid to a temperature below its melting point to bring about a state of thermal decomposition or a phase transition other than melting. (73)

DCP

Dicalcium Phosphate Dihydrate, $CaHPO_42H_2O$.

Dry Process Phosphoric Acid

Phosphoric acid made from elemental phsophorus. Also called furnace acid.

Eutectic

The lowest or highest melting point of an alloy or solution of two or more substances that is comprised of the same components. (73)

Ferrophosphorus

A by-product iron-phosphorus alloy of phosphorus smelting, typically containing 59 percent iron and 22 percent phosphorus. Symbolized as Fe_2P in this report.

Flux

A substance that promotes the fusing of minerals or metals or prevents the formation of oxides. For example, metal refining lime is added to the furnace charge to absorb mineral impurities in the metal. A slag is formed which floats on the bath and is run off. (73)

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Furnace Acid

Phosphoric acid made from elemental phosphorus. Also called dry process phosphoric acid.

Gangue

The minerals and rock mined with a metallic ore but valueless in themselves or used only as a by-product.(73)

Hydrolysis

A chemical reaction in which water reacts with another substance to form one or more new substances.(73)

Immiscible

The property of one liquid being unable to mix or blend uniformly with another.

l

liter.

MCP

Monocalcium Phosphate Monohydrate, $Ca(H_2PO_4)_2 - H_2O$.

Nodule

Semi-fused agglomerated and calcined phosphate rock particle.

Pdt

Product.

Phosphorus Mud

Sludge or emulsion of phosphorus, dust and water.

Phosphorus Oxychloride

$POCl_3$.

Phosphorus Pentasulfide

P_2S_5.

Phosphorus Pentoxide

P_2O_5.

Phosphorus Trichloride

PCl_3.

Phossy Water

Water containing colloidal phosphorus.

Process Water

Any water which, during the manufacturing process, comes into direct contact with any raw material, intermediate product, by-product, waste product or finished product.

Slag

The fused agglomerate which separates in metal smelting and floats on the surface of the molten metal. Formed by combination of flux with gangue of ore, ash of fuel, and perhaps furnace lining. The slag is often the medium by means of which impurities may be separated from metal. (73).

STP

Sodium Tripolyphosphate, $Na_5P_3O_{10}$.

TCP

Tricalcium Phosphate, $Ca_3(PO_4)_2$.

Transport Water

(1) Water used to carry solids from a site in a slurry form.

(2) Water accompanying a chemical in transport which is either immiscible with water or highly insoluble in water. The water acts as a blanket preventing contact of air or other substances with the chemical.

Wet Process Phosphoric Acid

Phosphoric acid made from phosphate rock and sulfuric acid.

TABLE 20

METRIC UNITS

CONVERSION TABLE

MULTIPLY (ENGLISH UNITS)		by	TO OBTAIN (METRIC UNITS)	
ENGLISH UNIT	ABBREVIATION	CONVERSION	ABBREVIATION	METRIC UNIT
acre	ac	0.405	ha	hectares
acre - feet	ac ft	1233.5	cu m	cubic meters
British Thermal Unit	BTU	0.252	kg cal	kilogram-calories
British Thermal Unit/pound	BTU/lb	0.555	kg cal/kg	kilogram calories/kilogram
cubic feet/minute	cfm	0.028	cu m/min	cubic meters/minute
cubic feet/second	cfs	1.7	cu m/min	cubic meters/minute
cubic feet	cu ft	0.028	cu m	cubic meters
cubic feet	cu ft	28.32	l	liters
cubic inches	cu in	16.39	cu cm	cubic centimeters
degree Fahrenheit	°F	0.555(°F-32)*	°C	degree Centigrade
feet	ft	0.3048	m	meters
gallon	gal	3.785	l	liters
gallon/minute	gpm	0.0631	l/sec	liters/second
horsepower	hp	0.7457	kw	killowatts
inches	in	2.54	cm	centimeters
inches of mercury	in Hg	0.03342	atm	atmospheres
pounds	lb	0.454	kg	kilograms
million gallons/day	mgd	3,785	cu m/day	cubic meters/day
mile	mi	1.609	km	kilometer
pound/square inch (gauge)	psig	(0.06805 psig +1)*	atm	atmospheres (absolute)
square feet	sq ft	0.0929	sq m	square meters
square inches	sq in	6.452	sq cm	square centimeters
tons (short)	ton	0.907	kkg	metric tons (1000 kilograms)
yard	yd	0.9144	m	meters

* Actual conversion, not a multiplier

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